

# THORPE'S DICTIONARY OF APPLIED CHEMISTRY

BY

(*the late*)

JOCELYN FIELD THORPE, Kt., C.B.E., D.Sc., F.R.S., F.I.C.

*Emeritus Professor of Organic Chemistry in the University of London  
and in the Imperial College of Science and Technology. Past  
President of the Chemical Society and of the Institute  
of Chemistry*

AND

M. A. WHITELEY, O.B.E., D.Sc., F.I.C.

*Lately Assistant Professor of Organic Chemistry, Imperial  
College of Science and Technology*

ASSISTED BY EMINENT CONTRIBUTORS

FOURTH EDITION (Revised and Enlarged)

VOL. VI

With an index to Vols. I—VI by Dr. J. N. Goldsmith

*WITH ILLUSTRATIONS*

LONGMANS, GREEN AND CO.

**LONGMANS, GREEN AND CO. LTD.**

**NICOL ROAD, BOMBAY**

**17 CHITTARANJAN AVENUE, CALCUTTA**

**36A MOUNT ROAD, MADRAS**

**FOURTH EDITION . . . 1913**



## FOREWORD.

THE first volume of the original edition of this Dictionary was published in 1890 under the editorship of Professor T. E. (later Sir Edward) Thorpe (Professor of Chemistry in the Normal School of Science and Royal School of Mines, South Kensington), who explained in the preface that the work is "*essentially a Dictionary of Chemistry in its Applications to the Arts and Manufactures; hence it deals but sparingly with the purely scientific aspects of Chemistry, unless these have some direct and immediate bearing upon the business of the technologist.*" The first edition occupied three volumes; the second and third editions, in five and seven volumes respectively, were also edited by Sir Edward Thorpe, but the third edition was still in course of publication at the time of his death in 1925. Seven years after its completion this edition was brought up to date by the publication, in 1934-36, of two supplementary volumes, together with a glossary and index. These were jointly edited by Professor J. F. (later Sir Jocelyn) Thorpe (Professor of Organic Chemistry and Director of Organic Chemistry Laboratories, Royal College of Science, Imperial College of Science and Technology, South Kensington) and Dr. Martha A. Whiteley (Assistant Professor of Organic Chemistry at the same college), thus maintaining the association of the Dictionary with the Chemistry Staff of the Royal College of Science.

The publication of a supplement was in itself insufficient to keep the Dictionary in line with the modern trend of applied chemistry, for the last one or two decades have shown clearly that pure science and technology, so tacitly distinguished in Sir Edward Thorpe's original preface, cannot be divorced. This changed attitude is reflected in the present edition of the Dictionary, of which Volumes I to VI inclusive have now been published under the above editorship. This edition is wider in scope than the preceding ones, and is intended to be a general work of reference for all who are concerned with various branches of chemistry and chemical industry.

The death of Sir Jocelyn Thorpe again made new editorial arrangements necessary. In order to maintain a balance between the various branches of chemical science an Editorial Board has been formed, comprising Professor I. M. Heilbron (Professor of Organic Chemistry and Director of the Laboratories for Organic Chemistry at the Imperial College) (Chairman), Dr. H. J. Emeléus (Assistant Professor and Reader in Inorganic Chemistry at the Imperial College), Professor H. W. Melville (Professor of Chemistry in the University of Aberdeen), and Professor A. R. Todd (Sir Samuel Hall Professor of Chemistry and Director of the Chemical Laboratories in the University of Manchester). This Board will determine the general editorial policy in conjunction with the publishers. Dr. Whiteley continues as Editor, and Dr. A. J. E. Welch (Assistant Lecturer in Inorganic Chemistry at the Imperial College) becomes Assistant Editor.

It is proposed to complete the current edition with seven further volumes, which it is hoped to publish at yearly intervals. Although the Board do not consider any major modification is called for in the general character of the work, they are of the opinion that certain changes in the scope of the articles will enhance its value.

Nowadays a great and growing part of applied chemistry involves a fundamental knowledge of physical chemistry. It is, therefore, felt desirable to increase the proportion of articles in this field. In the view of the Board this important addition can be achieved without increase in the number of volumes by the judicious selection of the subject matter, and the pruning of historical material. Twenty articles on physico-chemical subjects are included in this volume and, so far as is possible, other articles in this category, supplementing those which have appeared in Volumes I to V, will be included in later volumes under modified titles.

Each subsequent volume will contain an index. An index of the first six volumes is included in the present volume: this has been prepared by Dr. J. N. Goldsmith, to whom thanks are due also for valuable assistance in proof-reading.

The editorial work of the Dictionary continues to be carried on in Cambridge, and grateful acknowledgment is made to the Management Committee of the University Chemical Laboratory for the accommodation and library facilities afforded for this purpose.

M. A. WHITELEY.

# LIST OF CONTRIBUTORS

## TO VOLUME VI.

- Professor N. K. ADAM, Sc.D., F.I.C., F.R.S., *Professor of Chemistry, University College, Southampton.* [INTERFACIAL ANGLES.]
- Professor C. O. BANNISTER, M.Eng., A.R.S.M., F.I.C. [GOLD, MOSAIC; GOLD, PURPLE.]
- G. BARGER, (Hon.)D.Sc., (Hon.)M.D., LL.D., F.R.S. (the late), *Professor of Medical Chemistry, University of Edinburgh.* [GRAMINE; GUARANA.]
- RICHARD M. BARRER, D.Sc.(N.Z.), Ph.D.(Cantab.), F.I.C., *Head of Department of Chemistry, Technical College, Bradford.* [HETEROGENEOUS REACTIONS.]
- R. P. BELL, M.A., B.Sc. [HALF VALUE PERIOD; HOMOGENEOUS CATALYSIS.]
- A. J. BERRY, M.A., *Fellow of Downing College and University Lecturer in Chemistry, Cambridge.* [INDICATORS.]
- J. W. BLAGDEN, M.A., Ph.D., F.I.C. (the late), *Late Head of Research Dept. and Director of Howards and Sons, Ltd., Ilford, Essex.* [cycloHEXANE; cycloHEXANOL.]
- WILLIAM BRADLEY, M.Sc., Ph.D., *Lecturer in Tinctorial Chemistry and Dyestuffs, College of Technology, The University of Manchester.* [HIRSUTIDIN; HIRSUTIN; IDAEN.]
- DONALD BURTON, M.B.E., D.Sc., F.I.C., *Chief Chemist, Messrs. Wm. Walker & Sons, Ltd., Rose Hill Tannery, Bolton.* [GLUE AND GLUE TESTING.]
- H. S. COLES, B.Sc., *Imperial Chemical Industries, Ltd.*, and P. H. SYKES, M.Sc., Ph.D., *Imperial Chemical Industries, Ltd.* [HYDROGEN.]
- M. CARLTON, *see* J. A. KITCHENER.
- A. H. COOK, D.Sc., D.I.C., *Lecturer in Organic Chemistry, Imperial College of Science and Technology, London, S.W.7.* [HYDRAZINES; HYDRAZONES; INDAMINES AND INDOPHENOLS; INDENE; INDOLES.]
- HENRY E. COX, Ph.D., D.Sc.(Lond.), F.I.C., *Consulting Chemist, London; see also* ELSA LEW-KOWITSCH. [HAIR DYES; HENNA.]
- E. J. CROSS, *see* A. G. PERKIN.
- GLYN R. DAVIES, Ph.D.(B'ham.), B.Sc.(Lond.), *Chemical Research Laboratory, Teddington, Mddx.* [GLUCINUM; HAFNIUM; HOLMIUM; ILLINIUM; INDIUM.]
- D. M. EGAN, *see* J. R. PARTINGTON.
- M. G. EVANS. [IDEAL OR PERFECT GAS.]
- CHARLES S. GIBSON, O.B.E., M.A., Sc.D., F.R.S., *Professor of Chemistry in the University of London at Guy's Hospital Medical School.* [GOLD, COMPOUNDS OF.]
- J. N. GOLDSMITH, Ph.D., M.Sc., F.I.C., 45 *Ashley Gardens, London, S.W.1.* [HELLEBORUS; HYDROGENATION ANALYSIS.]
- R. F. GOLDSTEIN, B.Sc., Ph.D., F.I.C., A.M.Inst.Pet., I.C.I. (Dyestuffs), Ltd., *Blackley, Manchester.* [INHIBITORS, ANTIOXIDANT.]
- G. C. HAMPSON, M.A., D.Phil. [INCONGRUENT MELTING POINT.]
- J. A. HANLEY, A.R.C.S., Ph.D., *Professor of Agriculture and Rural Economy, King's College, Newcastle-on-Tyne.* [GRASS LAND.]
- E. F. HARTREE, M.A., Ph.D. [HEMIN.]
- ARTHUR HEATH. [GLAZES AND FRITS.]

- Professor I. M. HELLBRON, D.S.O., (Hon.) LL.D. (Glas.), D.Sc., F.R.S., *Professor of Organic Chemistry in the University of London (Imperial College), Imperial College of Science and Technology, South Kensington, London, S.W.7, and F. S. SPRING, Ph.D., D.Sc., Senior Lecturer in Chemistry, The University, Manchester.* [GLYCIMERIN; HELENIEN.]
- Dr. N. F. M. HENRY. [GONIOMETRIC.]
- J. T. HEWITT, A.R.C.S., M.A., D.Sc., Ph.D., F.R.S., *Emeritus Professor of Chemistry, Queen Mary College, London.* [HYDRINDONE.]
- W. H. HOFFERT, M.A., B.Sc., F.I.C., *Chief Chemist, National Benzole Company Limited.* [INHIBITORS; GUM.]
- R. HOLROYD, M.Sc., Ph.D., *I.C.I. (Fertilizer and Synthetic Products), Ltd., Billingham.* [HYDROGENATION OF COAL.]
- Professor C. K. INGOLD, F.R.S. [INDUCTIVE EFFECT.]
- J. A. KITCHENER, B.Sc., Ph.D., *Assistant Lecturer in Inorganic and Physical Chemistry, Imperial College of Science and Technology, London, S.W.7;* and M. CARLTON, B.Sc., Ph.D., *Imperial College of Science and Technology, London, S.W.7.* [HYDROGEN PEROXIDE.]
- G. A. R. KON, M.A. (Cantab.), D.Sc. (Lond.), F.R.S., *Professor of Chemistry, Chester Beatty Research Institute, Royal Cancer Hospital (Free), London, S.W.3.* [HORMONES.]
- ELSA LEWKOWITSCH, Ph.D., D.I.C., *Lewkowitsch Laboratory, 71 Priory Road, N.W.6.* [GRAPE-SEED OIL; GREASES; HAZEL NUT OIL; HEDGE-MUSTARD OIL; HEMPSEED OIL; HORSE FAT; HYENIC ACID; INSECT WAX; INUKAYA OIL.]
- ELSA LEWKOWITSCH and H. E. COX. [GLYCERIN.]
- W. H. LINNELL, M.Sc., D.Sc., Ph.D., F.I.C. [HENBANE.]
- M. C. MARSH, M.A. (Cantab.), Ph.D. (Lond.), F.Inst.P., *Research Department, Cambridge Instrument Co., Ltd., Cambridge.* [HUMIDITY AND HUMIDITY CONTROL.]
- GEO. MARTIN, B.Sc., F.I.R.I., *Superintendent of Rubber Investigations, London Advisory Committee for Rubber Research (Ceylon and Malaya), Imperial Institute, London, S.W.7.* [GUTTA PERCHA AND BALATA.]
- Dr. FREDERICK A. MASON, M.A. (Oxon.), Ph.D. (Munich), F.I.C.,  *sometime Lecturer in Dyestuffs and Tinctorial Chemistry, Municipal College of Technology, Manchester.* [INDULINEN.]
- C. AINSWORTH MITCHELL, M.A., D.Sc. (Oxon.), F.I.C., *Consulting Chemist, Editor of "The Analyst"; see also K. A. WILLIAMS.* [INDIAN OR CHINESE INK; INK.]
- D. M. NEWITT, F.R.S., *Imperial College of Science and Technology, London, S.W.7.* [HIGH PRESSURE REACTIONS.]
- ERNEST J. PARRY, D.Sc. (Lond.), F.I.C., *of Gray's Inn, Barrister-at-Law.* [GLYCIDIC ESTERS; GUAIACUM RESIN; GUAIYL ACETATE; GUMS; GURJUN BALSAM; HAWTHORN PERFUME; HELIOTROPE PERFUME; HELIOTROPIN; HEPTALDEHYDE; HEPTYL ALCOHOL; HEXALDEHYDE; HEXYL ALCOHOL; HONEY-SUCKLE PERFUME; HYACINTH, ARTIFICIAL; HYDROQUINONE ETHERS; HYDROXYCITRONELLAL; INDOLE.]
- J. R. PARTINGTON, M.B.E., D.Sc., *Professor of Chemistry, University of London,* and Miss D. M. EGAN, B.Sc. [HITTOFF TRANSPORT (OR TRANSFERENCE) NUMBER; HYDRATION OF IONS.]
- A. G. PERKIN, D.Sc., F.I.C., F.R.S.E., F.R.S. (the late), *Emeritus Professor of Colour Chemistry and Dyeing, University of Leeds.* Articles revised by E. J. CROSS, Ph.D., *Lecturer in Colour Chemistry, University of Leeds.* [GREEN EBONY; HEATHER; INDIAN YELLOW.]
- A. G. POLLARD, B.Sc., A.R.C.S., D.I.C., F.I.C., *Lecturer in Agricultural Chemistry, Imperial College of Science and Technology, London, S.W.7.* [GOOSEDERBY; GORSE; GRAPE; GRAPE-FRUIT; GROUND NUT; GROWTH PROMOTING SUBSTANCES; HAWTHORN; HONEWORT; HONEY; HORSE CHESTNUT; HORSE RADISH; HUCKLEBERRY; HUMIC ACID; ICACO.]
- ARTHUR DUDLEY POWELL, F.I.C., *Chief Analyst, Boots Pure Drug Co., Ltd., Beeston.* [HAMAMELIN; HAMAMELIS.]
- R. H. PURCELL, Ph.D., D.I.C., *Lecturer in Physical Chemistry, Imperial College of Science and Technology, London, S.W.7.* [HYDROGEN ION DETERMINATION.]
- F. L. PYMAN, Ph.D., D.Sc., F.I.C., F.R.S., *Director of Research, Boots Pure Drug Co., Ltd., Nottingham.* [HYDRASTINE.]
- J. H. QUASTEL, D.Sc. (Lond.), Ph.D. (Cantab.), A.R.C.S., F.I.C., F.R.S., *Director: Agricultural Research Council Unit of Soil Biochemistry, Rothamsted Experimental Station, Harpenden.* [GLYCOLYSIS.]
- E. H. RODD, A.C.G.I., D.Sc., F.I.C., *I.C.I. (Dyestuffs), Ltd., Blackley, Manchester.* [INDIGO, NATURAL AND SYNTHETIC; INDIGOID DYESTUFFS; INDOXYL COMPOUNDS.]

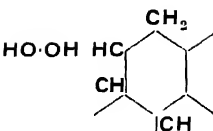
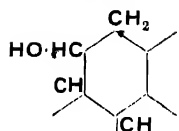
- SIR THOMAS KIRKE ROSE, A.R.S.M., D.Sc. [GOLD.]
- W. HUME-ROTHERY, M.A., D.Sc., F.R.S., *Fellow of Magdalen College, Oxford.* [HUME-ROTHERY'S RULE.]
- H. N. RYDON, D.Sc.(Lond.), D.Phil.(Oxon.), A.R.C.S. [GLUTACONIC ACID; GLUTARIC ACID; HYDROGENATION.]
- EMIL SCHLITTLER, Dr.-Ing.(Zuerich), Ph.D.(Edin.). [GLAUCINE; HARMALA; HEDYOTINE; HORDENINE; BOGAINE; INSULARINE.]
- DR. J. L. SIMONSEN, F.R.S., *Director of Research, Colonial Products Research Council, Imperial Institute, South Kensington, S.W.7.* [GLOBULOL; GUAJOL; GURJURENES.]
- L. J. SPENCER, C.B.E., M.A., Sc.D., F.R.S., *Editor of the "Mineralogical Magazine," formerly Keeper of Minerals in the British Museum.* [GLAUCONITE; GOETHITE; GOSLARITE; GRANITE; GREENALITE; GREEN-EARTH; GREENOCKITE; GUDMUNDITE; GUMMITE; GYPSUM; HÆMATITE or HEMITE; HALITE; HALLOYSITE; HALOTRICHITE; HAUSMANNITE; HELLANDITE; HEMIMORPHITE; HERZENBERGITE; HESSITE; HEWETTITE; HIDDENITE; HILGARDITE; HOLLANDITE; HOPEITE; HORNBLEND; HORNSTONE; HULSITE; HUTCHINSONITE; HYACINTH or JACINTH; HYDROCERUSSITE; HYDROMAGNESITE; HYDROZINCITE; HYPERSTHENE; IANTHINITE; IDOCRASE; ILMENITE; ILVAITE; IDERITE.]
- F. S. SPRING, *see* I. M. HEILBRON.
- J. J. SUDBOROUGH, Ph.D., D.Sc., F.I.C., *Formerly Professor of Organic Chemistry in the Indian Institute of Science, Bangalore, India.* [HYDROLYSIS.]
- G. B. B. M. SUTHERLAND, M.A., B.Sc., Ph.D., *Fellow and Lecturer, Pembroke College, Cambridge.* [INTERATOMIC DISTANCES.]
- P. H. SYKES, *see* H. S. COLES.
- W. V. THORPE, M.A., Ph.D., *Reader in Chemical Physiology, University of Birmingham.* [HYPOXANTHINE.]
- A. R. TODD, D.Sc., D.Phil., F.I.C., F.R.S., *Sir Samuel Hall Professor of Chemistry and Director of the Chemical Laboratories, Manchester University.* [INDIAN HEMP RESIN.]
- G. H. TWIGG, B.Sc., Ph.D., *Department of Colloid Science, Cambridge University.* [HYDROGENATION MECHANISM.]
- A. J. E. WELCH, Ph.D., A.R.C.S., D.I.C., *Assistant Lecturer in Inorganic Chemistry, Imperial College of Science and Technology, London, S.W.7.* [HELIUM.]
- MARTHA A. WHITELEY, O.B.E., D.Sc., F.I.C. [GLUTAMIC ACID; GLUTAMINE; GUANINE; HYDANTOIN; HYDURILIC ACID.]
- K. A. WILLIAMS, B.Sc.(Lond.), F.I.C., *Consulting and Technical Chemist, 4 and 6 Malver Street, London, S.W.3, and C. AINSWORTH MITCHELL.* [HARDENED OR HYDROGENATED FATTY OILS.]
- G. T. YOUNG, B.Sc., Ph.D., A.I.C., *Lecturer in Organic Chemistry, University of Bristol.* [GLYCOSIDES; HEMICELLULOSES; INOSITOL; INVERTASE.]

## NOTE

*Italicised words in inverted commas may be registered trade names*



## ERRATA.

<i>Vol.</i>	<i>Page</i>	<i>Line</i>	<i>For</i>	<i>Read</i>
II	442c	14	* <i>Niger</i>	<i>viridis</i>
II	455d	15*	oxide	acid
II	520a	23	<i>azulene (q.v.)</i>	<i>chamazulene</i>
II	520a	34	azulene	chamazulene
II	529c	(Formula A.)		
II	533b	1*	Pó lányi	Polanyi
II	564c	5	<i>Delete carbonate,</i>	
II	667b	6*	1935	1933
III	6d	7*, 6*	scale suffices	scale. The accuracy suffices
III	50d	16*	essential	essentially
IV	5d	17*	METHYLPHENYL-METHANE	METHYLDIPHENYL-METHANE
IV	8c	9	Lovery	Lovercy
IV	29c	35	<i>cresol</i>	<i>cresol</i>
IV	191c	23	<i>p</i> -phenylenediamine	<i>m</i> -phenylenediamine
IV	211c	25-27	<i>Delete</i> For this reason, these forms of dynamite have not been authorised for use in England.	
IV	249d	15*	flushed	flushed
IV	316a	1	<i>oryza</i>	<i>oryza</i>
IV	325c	9	cryptograms	cryptogams
IV	358a	17	230	320
IV	361b	33*	H(CO) <sub>3</sub> (NEt) <sub>2</sub>	NH(CO) <sub>3</sub> (NEt) <sub>2</sub>
IV	366b	3*	EO-OH	EtO-OH
IV	373a	30	Durrano	Durrant
IV	487b	28*	<i>Grisou</i>	<i>Grisou</i>
IV	499c	20	317	517
IV	575a	13	2	11
IV	590a	17	<i>Fakis</i>	<i>Faktis</i>
V	vii	14	<i>Brook</i>	<i>Brock</i>
V	306c	33	303g	303a
V	327d	24*	FORMOMONETIN	FORMONONETIN
V	519c	11	SESAMINE	SESAMÉ
V	588	(Fig. 33, title)	DAMP	LAMP
VI	119b	11*	" <i>Allochrysin</i> "	" <i>Allochrysine</i> "
VI	300d	24*	" <i>antipyrrine</i> "	" <i>antipyrrin</i> "
VI	302b	7*	" <i>antipyrrine</i> "	" <i>antipyrrin</i> "
VI	418c	22	<i>Hydrc</i>	<i>Hydron</i> •



# A DICTIONARY OF APPLIED CHEMISTRY.

G—continued.

GLAUBERITE (v. Vol. II, 233c).

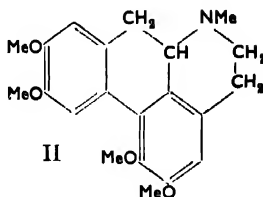
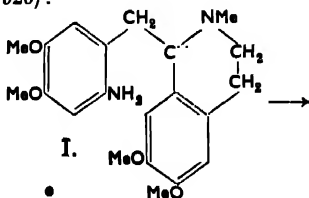
GLAUCANIC ACID (v. Vol. V, 56b).

GLAUCIC ACID (v. Vol. V, 56b).

GLAUCINE,  $C_{21}H_{22}O_4N$ , occurs in several plants of the Papaveraceæ and Fumariaceæ family. It was first isolated from *Glaucium luteum* by Probst (Annalen, 1839, **31**, 241) and from the same plant along with protopine by R. Fischer (Arch. Pharm. 1901, **239**, 426). Since then glaucine has been isolated from *Corydalis tuberosa* (Gadamer, *ibid.* 1911, **249**, 224), *Dicentra erimia*, *D. formosa* and *D. oregana* (Manske, Canad. J. Res. 1933, **8**, 592; 1934, **10**, 521, 765; 1937, **15**, B, 274). Ordinary glaucine is dextrorotatory; Go (J. Pharm. Soc. Japan, 1930, **50**, 122 or Chem. Zentr. 1931, **1**, 791) claims to have obtained *l*-glaucine from a Korean corydalis.

Extraction of glaucine from *Glaucium luteum*, see Barger and Silberschmidt, J.C.S. 1928, 2923. The base was first prepared in a pure state and characterised by R. Fischer (*l.c.*). It crystallises in colourless rhombic prisms or bundles of needles, m.p. 119–120°,  $[\alpha]_D^{20} +113^\circ$  (in EtOH). The base is soluble in the usual organic solvents, as a non-phenolic aporphine base (for definition, see Gadamer *et al.*, Arch. Pharm. 1925, **263**, 81); it is also soluble in light petroleum. The salts are crystalline, although they may precipitate as jellies (especially the hydrochloride). Apart from its natural source, glaucine has been obtained from *laurotetanine*, *N*-methyl*laurotetanine*, *boldine* and *glaucentrine* by methylation (Barger and Silberschmidt, *l.c.*; Späth and Strauhal, Ber. 1928, **61** [B], 2398; Späth and Suominen, *ibid.* 1933, **66** [B], 1344; Wernat, *ibid.* 1925, **58** [B], 2768; *ibid.* 1926, **59** [B], 85).

Glaucine has been synthesised by Gadamer (Arch. Pharm. 1911, **249**, 680) by treating a diazotised solution of aminolaudanoline (I) with copper powder, when phenanthreno-*N*-methyl-tetrahydropapaverine (II), identical with *dl*-glaucine, was formed (see also Paschorr, Ber. 1904, **37**, 1926):



Like all racemic aporphine bases, *dl*-glaucine can easily be resolved into the optically active compounds by means of the *d*- and *l*-tartaric acids.

Glaucidine, m.p. 238–239° (decomp. starting at 209–210°) has been isolated from *Papaver orientale* (Klee, Arch. Pharm. 1914, **252**, 274); it is believed to be closely related to glaucine.

Glaucentrine,  $C_{17}H_{13}N(OH)(OMe)_3$ , m.p. 148° has been isolated from *Dicentra erimia* (Manske, Canad. J. Res. 1938, **16**, 81). By methylation with diazomethane glaucine is obtained. Glaucine is said to induce narcosis accompanied by some tetanising action.

Schl.

GLAUCOBILIN (v. Vol. I, 691c).

GLAUCONIC ACID (v. Vol. V, 56b).

GLAUCONITE. (*Glaucanie*, Fr.; *Glaukonit*, Ger.) Hydrated silicate of iron, potassium, etc., of variable composition, found as small rounded grains in sedimentary rocks. It was named in 1828, from *γλαυκός*, bluish-green, on account of its characteristic colour, which is of various shades of dark green. The typical occurrence of the mineral is the Greensand formation (below the Chalk) of the Cretaceous system, but it is also met with in sands, sandstones, marls and limestones of all ages from the Cambrian, and is forming at the present day on the floor of the ocean. The granules measure about  $\frac{1}{2}$  to 1 mm. in diameter. Under the microscope they show a clear green or yellowish-green, slightly pleochroic and birefringent material embedded in a network of black, optically isotropic, organic matter, the latter having the composition of humic acid. The mineral is decomposed by hot concentrated hydrochloric acid, and before the blowpipe it is fusible with difficulty to a black magnetic slag.

Analysis I is of grains isolated from a calcareous sandstone in the Upper Greensand at Woodburn, Carrickfergus, Co. Antrim (A. P. Hoskins, Geol. Mag. 1895). II, from the Cambridge Greensand (G. D. Liveing, Geol. Mag.

1866). III gives the extreme values shown in ten analyses of glauconite grains isolated from Eocene, Cretaceous, and Jurassic sandstones and from Lower Silurian limestone from various Russian localities; sp.gr. 2.40–2.87, varying like the colour—yellowish-green and dark green—with the percentage of iron (K. D. Glinka, 1896). IV, grams forming 83% of a sandy deposit dredged at a depth of 556 fathoms from the Pacific off Panama (W. A. Caspari, Proc. Roy. Soc. Edin. 1910, 30, 364). V, similar material dredged at 110 fathoms from the Agulhas Bank, South Africa (W. A. Caspari, *l.c.*). Numerous analyses of glauconite are quoted by C. K. Leith, Monographs, U.S. Geol. Survey, 1903, 53, 240. Analyses of Swedish glauconites, by N. Sahlbom, Bull. Geol. Inst. Univ. Upsala, 1916, 15, 211; A. Hudding, Lunds Univ. Årsskrift, 1932, 28, No. 2.

	I.	II.	III.		IV.	V.
			Min.	Max		
SiO <sub>2</sub> . .	40.00	51.09	41.02	52.96	40.12	51.15
Al <sub>2</sub> O <sub>3</sub> . .	13.00	9.00	5.84	22.19	7.09	7.61
Fe <sub>2</sub> O <sub>3</sub> . .	16.81	—	8.17	23.13	25.95	18.83
FeO . .	10.17	19.54	1.32	5.95	0.89	2.78
MgO . .	1.07	3.37	0.69	4.11	3.10	4.54
CaO . .	1.07	0.30	—	8.37	—	—
Na <sub>2</sub> O . .	2.16	3.56	0.30	0.98	—	—
K <sub>2</sub> O . .	8.21	2.47	5.74	9.54	7.02	7.80
H <sub>2</sub> O . .	6.19	10.80	4.45	7.88	7.12	7.56
	100.48	100.13	—	—	100.29	100.27

The chemical composition has been discussed and a variety of formulae deduced by A. F. Hallimond, Min. Mag. 1922, 19, 330; C. S. Ross, Proc. U.S. Nat. Mus. 1926, 69, art. 2; H. Schneider, J. Geol. 1928, 13, 589; A. Hudding, *l.c.*; J. W. Gruner, Amer. Min. 1935, 20, 699; K. Smulikowski, Arch. Min. Soc. Sci. Varsovie, 1936, 12, 145. Closely allied to glauconite are the minerals celadonite (green-earth) and greenalite (this vol., p. 135d).

The Greensand of England, consisting mainly of sandy beds with quartz grains intermixed with glauconite, is developed in the Wealden area, the Isle of Wight, and extends from Berkshire and Oxfordshire to Norfolk and Lincolnshire. Some of the limonitic iron-ores of these districts may possibly, like those of the Lake Superior region, have been derived by the alteration of glauconite. The same formation has also a wide distribution on the Continent. In America, greensand and glauconitic marls of Cretaceous and Tertiary age are developed in New Jersey, Virginia, Kentucky and Tennessee. The glauconite marls of New Jersey contain K<sub>2</sub>O 1.54–7.08% with P<sub>2</sub>O<sub>5</sub> 0.19–6.87%, and have been extensively used in the raw state as an agricultural dressing (*v.* Ann. Rep. State Geologist New Jersey, 1886, 1892, 1893). Those from Virginia have been used in the preparation of commercial fertilisers. Attempts have been made to extract potash from greensands (U.S. Geol. Survey, Min. Res. for 1911, 1912, ii, 901).

The frequent association of phosphatic nodules with glauconite deposits has some bearing on the origin of glauconite. The terrigenous deposits of green mud and sand formed on the floor of

the ocean at depths of about 200 to 1000 fathoms, and found by the "Challenger" Expedition to be of wide distribution, particularly off continental coast lines composed of igneous rocks, contain this mineral in considerable amount. The potash set free by the weathering of the feldspars and micas of these rocks and carried into the sea is conserved by the formation of glauconite, but apparently only through organic agencies, which at the same time give origin to the phosphatic nodules. Grains of glauconite are frequently found filling the chambers of foraminifera and other organisms; and in the artificial production of the mineral the presence of an organic acid seems to be essential (W. A. Caspari, *l.c.*). E. W. Galliher (Bull. Geol. Soc. Amer. 1935, 46, 1351) gives analyses showing the gradual alteration of biotite to glauconite in Monterey Bay, California, and suggests that the alteration is due to sulphur bacteria in the black mud and alkaline sea-water.

L. J. S.

**GLAZES AND FRITS.** In the ceramic industry the term "glaze" is intended to convey a vitreous coating fixed by heat on the underlying pottery body.

Pottery bodies cover a very wide range of articles made from clay, which when fired give a hard mass, but, except in the case of clays which of themselves give, when fired, a perfectly vitreous surface, remain of a porous nature and readily absorb moisture, and consequently are unsuited to domestic requirements. It becomes necessary, therefore, after the first fire, when the ware is in what is termed the "biscuit state," to affix to it a coating which, on being again subjected to heat, will render it impermeable to moisture and impart a smooth and glossy surface.

The term "glaze," however, while being understood to refer to this vitreous coating, is also applied to the mixture of ground materials used in the compounding of such glaze, and which mixture may be either in the form of a dry powder or an emulsion of these materials suspended in water. The terms used for these two varieties are "dry glaze" and "slop glaze," and these are often supplied to potters by "millers" specially equipped for their manufacture. The potters thus avoid the trouble of making small quantities in their own works.

Glazes broadly may be divided into three classes, viz., transparent, opaque and coloured, but all must fulfil certain conditions, viz.:

- (1) Must be sufficiently hard to resist abrasion.
- (2) For domestic use should be resistant to the action of ordinary acids.
- (3) Must be sufficiently fusible to adhere firmly to the body without subjecting this to any undue risk of warping during fire, but sufficiently infusible to prevent running off the biscuit ware during the firing of the glaze.
- (4) Must have approximately the same coefficient of expansion as the body, to prevent the risk of either of the two main faults of glazes, viz., crazing and peeling.
- (5) Must hold dissolved, without unsightly separations, metallic oxides that have been added to impart colour.

(6) Must not exert too strong a solvent action on the colours used in painting and decoration of the ware.

The difficulties attending the fulfilment of such varied conditions therefore necessarily involve much careful study and research work by the potter, and having regard to the many varieties of bodies used and the conditions appertaining to the methods of compounding both the body and also the glaze, and the methods of firing, the published recipe of any glaze is of very little practical service unless accompanied by an accurate description of the body on which it is applied, and the many other factors involved. Much general information may, however, be obtained by a knowledge of the fundamental principles involved and the materials available to produce the desired result.

At first sight glass seems to have some of the required properties, but when fired on the body it yields a devitrified mass scarcely sintered together. It becomes evident then, that what is required is something which, while still of a glassy nature, needs additions of other materials to render it of service. Ordinary flint glass consists of silica, soda, lime and lead, and using these materials as a basis of experiment, the necessary additions and alterations can be made to bring about the desired result.

The composition of glazes varies within very wide limits according to the maximum temperature required to mature them, the duration of the firing and the nature of the body on which they are fired. The fusion point of a glaze depends on the nature of the ingredients used as well as on the relative quantities employed. All glazes may be looked upon as glasses, and their fusing points will depend largely on the ratio of the basic compounds to the acidic content in the formation of silicates or borosilicates and also on the alumina content.

A convenient method of expressing the composition is in terms of the chemical formula which shows at a glance the relative molecular proportions of the different oxides present, the alumina being kept separate and the silica and boric acid being classed as the acidic content.

Usually the bivalent basic oxides are collectively classed as RO, the whole being taken as one molecular proportion, then the alumina being placed as intermediary, followed by the acids (silica and boric acid). Such method enables easy comparison of the large number of recipes in existence which themselves give little indication of the true properties, and also enables the potter to see at a glance the possibility of substituting other materials for those called for in the recipe with the assurance of maintaining the necessary equilibrium of the finished glaze. A simple example will illustrate the application of this principle.

A recipe for a glaze is given as white lead 258, china clay 52 and flint 81 parts.

Assuming all the materials to be pure and having the formulæ :

	Mol. wt.
White lead, $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$ . . . . .	775
China clay, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . . . . .	258
Flint, $\text{SiO}_2$ . . . . .	60

a simple calculation gives the formula of the glaze as  $\text{PbO} : 0.2 \text{ Al}_2\text{O}_3, 1.75 \text{ SiO}_2$ . Such a glaze would mature at a relatively low temperature, approximately  $900^\circ\text{C}$ .

Generally speaking, the maturing point of a glaze may be said to be governed by :

(1) The equivalent proportion between acids and bases.

(2) The proportion of alumina in relation to the bases and acids.

(3) The ratio between the silica and boric acid. The higher the silica content of the glaze, the less fusible it becomes, therefore the modification of the proportion of silica in a glaze affords an easy means of regulating its fusibility.

Expressed in the foregoing manner, the whole range of glazes in common use fall within the following limits :

#### Common Pottery.

RO : 1.5  $\text{SiO}_2$  to RO : 3  $\text{SiO}_2$

#### Earthenware, Bone China and Stoneware.

RO : 0.25  $\text{Al}_2\text{O}_3$ , 2.5  $\text{SiO}_2$

to RO : 0.40  $\text{Al}_2\text{O}_3$ , 4.5  $\text{SiO}_2$

#### Porcelain.

RO : 0.5  $\text{Al}_2\text{O}_3$ , 5.0  $\text{SiO}_2$

to RO : 1.25  $\text{Al}_2\text{O}_3$ , 12.0  $\text{SiO}_2$

with firing temperatures ranging from  $900$ – $1,450^\circ\text{C}$ .

Glazes fall conveniently into four groups according to composition, viz. :

(1) *Alkaline*, which are mainly silicates of the alkalis or of alkalis and lime.

(2) *Felspathic*, consisting of silica, alumina and alkalis and containing a large proportion of felspar or felspathic rock.

(3) *Lead*, consisting mainly of silicates and borosilicates, of alkalis and alkaline earths with some alumina and softened by addition of lead oxide and boric acid.

(4) *Enamels or opaque glazes*, which are usually of similar composition to lead glazes, but rendered opaque by the addition of opacifying agents such as tin oxide, arsenious oxide, zirconia, etc.

**Alkaline Glazes.**—The simplest example of the first type of glaze, i.e. the alkaline, is the well-known *salt glaze* used extensively on stoneware, but also formerly applied to earthenware which, when fired, is essentially an alkali-alumina silicate. It is produced in practice by the introduction of common salt into the kiln when the ware is near its vitrifying point. The vapour of the salt accompanied by steam decomposes the salt into sodium oxide and hydrochloric acid, the former entering into combination with the silica, alumina and basic compounds of the clay to form a sodium alumina glass very rich in silica. A very good salt glaze, after firing, approximates to the formula :

RO : 0.5  $\text{Al}_2\text{O}_3$ , 4.0 to 8.0  $\text{SiO}_2$

As the salt gives only the one constituent, viz. :  $\text{Na}_2\text{O}$  to the RO content, it is evident that the remainder of the formula must be taken up from the body.

It is also essential that the body shall possess the alumina and silica in such a ratio as to give

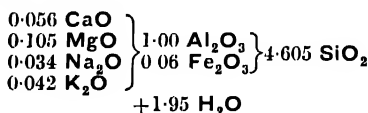
## GLAZES AND FRITS.

the most stable glaze. The body also must contain sufficient fluxing material to become vitreous at a reasonable heat, for if the body be still porous when the alkali fumes are introduced in the kiln, these will be absorbed by the clayware without glazing the surface.

Much research work has been done with a view to finding the best relations between the constitution of a clay and its ability to form a good salt glaze. L. E. Barringer (Trans. Amer. Ceram. Soc. 1902, 4, 211) proves that, contrary to some expressed opinions, it is essential that the clay shall have a certain alumina-silica ratio to be capable of giving a good salt glaze. He gives the analysis of the clay used, and also of the glaze, taken from fired specimens of what is known as a first class salt-glaze product.

Clay analysis.	
SiO <sub>2</sub>	63.11
Al <sub>2</sub> O <sub>3</sub>	23.30
Fe <sub>2</sub> O <sub>3</sub>	2.235
CaO	0.725
MgO	0.970
Na <sub>2</sub> O	0.490
K <sub>2</sub> O	0.930
SO <sub>3</sub>	0.240
H <sub>2</sub> O	7.810
	<hr/> 99.810 <hr/>

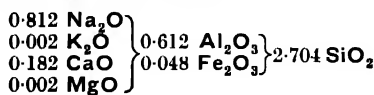
corresponding to the formula :



and the glaze gave

SiO <sub>2</sub>	55.475
Al <sub>2</sub> O <sub>3</sub>	21.340
Fe <sub>2</sub> O <sub>3</sub>	2.640
CaO	3.500
MgO	0.040
Na <sub>2</sub> O	17.210
K <sub>2</sub> O	0.080
	<hr/> 100.285 <hr/>

corresponding to the formula :

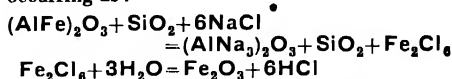


RO = 0.998

It will be noticed that for the clay, Al<sub>2</sub>O<sub>3</sub> is taken as unity, while in the glaze the sum of the bases RO is taken as unity, following the practice usually adopted in ceramic calculations. This particular clay is thus seen to have an Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> ratio of 1:4.6.

From further experiments recorded in the same work the author still got a good salt glaze, by the addition of free silica to the original clay up to the ratio Al<sub>2</sub>O<sub>3</sub> to SiO<sub>2</sub> 1:10.

Knell (Tonind-Ztg. 1896, 20, 495) assumed that the salt vapour attacked a double silicate of aluminium and iron in the body; the sodium of the salt displaced the iron of the double silicate; and the salt glaze remained behind as a double silicate of aluminium and sodium. The iron was supposed to be liberated as ferrie chloride which, in contact with water vapour in the oven, was transformed into ferric oxide and hydrogen chloride. He gives the reactions occurring as :



But this view meets with little approval, as the quantity of iron present in the clay body exposed to the action of the salt fumes is too small to account for the amount of glaze formed.

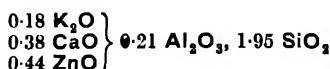
It is quite evident, however, that the salt vapour, in attacking the silica and alumina of the body, will have its effect on the iron content of the clay according to the amount of iron present, and also to the nature of the fire just prior to salting, as in the event of this being "reducing," the iron will be reduced to the ferrous state and give to the finished glaze a much darker colour than if an oxidising atmosphere had been maintained throughout the firing and glazing. While salt glaze is mainly used in the stoneware industry, it is interesting to note that in the early eighteenth century much fine earthenware of a good white colour was glazed by this process, but it was entirely abandoned with the advent of lead glazes.

The chief advantage of salt glaze is its high resistance to the action of acids and this property has led to its extensive use in the manufacture of articles for the chemical industry.

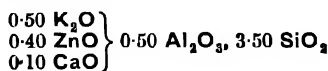
In applying the salt glaze the ware is placed in the kiln with the surfaces to be glazed exposed to the kiln atmosphere. When the temperature corresponding to the vitrifying stage of the clay ware is reached and a clear fire maintained, a quantity of salt is thrown in the fire-holes; this decomposes in the kiln with a lowering of the temperature inside the kiln of about 100°C. The fires are then fed to restore the temperature to the desired level and a further batch of salt introduced; the same procedure may be repeated three or four times according to the quantity of salt used in each application and the composition of the body. After the last salt application, the reheating is repeated until the maximum temperature is reached, approximately 1,250°C., when the kiln is allowed to cool.

It has been suggested (Everhart, J. Amer. Ceram. Soc. 1930, 13, 401) that the salt, instead of being applied by the foregoing method, can be utilised as a glaze when embodied in a slip and dipped on the ware in the usual way. A clay slip made from the same material as the body offers the ideal medium for introducing the salt. A mixture of 75 clay to 25 salt ground together and applied either by dipping or spraying and fired to about 1,150°C. gives a nice smooth surface. This method does not seem to have passed the experimental stage, but the results so far obtained are quite satisfactory. Coloured slips may also be used with good effect.

**Felspathic Glazes.**—This type covers the range usually termed Bristol Glazes which are of a felspathic type and maturing at a high temperature, 1,250–1,300°C. They are of two varieties—transparent and opaque—and mainly used on stoneware and glazed bricks. In this type a representative formula for a transparent glaze would be: (N. D. Wood, Trans. Ceram. Soc. 1935, 34, 279)

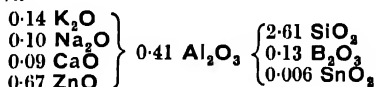


the raw materials usually adopted being felspar, whiting, zinc oxide, china clay and flint, whereas the opaque variety is produced by varying the proportions of the same raw materials and adding an opacifying agent such as tin oxide, zirconia, arsenious oxide, bone ash, etc. Such glazes approximate to the formula:

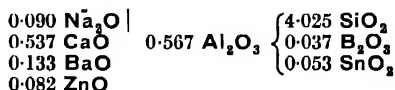


These glazes possess the advantage of cheapness, no fritting being required, but they do not give a very brilliant surface, so that for the better classes of stoneware (domestic and art ware) a fritted leadless-glaze is usually adopted with the approximate formula as follows:

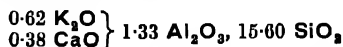
*Frit*



*Glaze* containing 3% of above frit

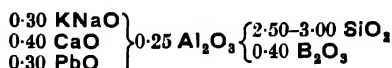


A felspathic glaze, as used in the production of hard porcelain, both Continental and English, with which the body is first fired at a low temperature, about 800°C., and then glazed and fired at a very high temperature (1,450–1,550°C.), would approximate to the formula:



The third group of glazes comprises those consisting mainly of silicates and boro-silicates with some alumina and softened by the addition of lead oxide; such include all ordinary English earthenware transparent glaze and also most of the English porcelains.

The best glazes in this group approximate to the formula:



and give a good clear transparent glaze when fired at about 1,150°C.

These glazes are usually compounded from a frit consisting of borax, whiting, flint, felspar and china clay, to which is added on grinding white lead, felspar or Cornish stone, china clay and flint.

A typical example of such a glaze is:

*Frit*

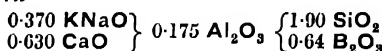
Borax . . . . .	37.7
Whiting . . . . .	18.8
Cornish stone . . . . .	18.8
Flint . . . . .	18.8
China clay . . . . .	5.6
	<hr/>
	99.7

*Glaze*

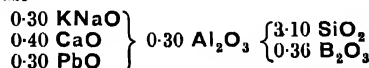
Frit . . . . .	36.8
Cornish stone . . . . .	31.8
Flint . . . . .	10.2
White lead . . . . .	21.2
	<hr/>
	100.0

giving formulae:

*Frit*



*Glaze*

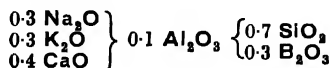


**Fritting.**—The limitations of raw glazes are so great by reason of the small number of materials available that in order to widen the field it is essential to resort to the process of fritting which accomplishes three objects:

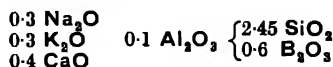
- (1) Makes a soluble substance insoluble.
- (2) Drives out volatile and useless substances in the original materials which otherwise would have to be done when the glaze is on the surface of the ware.
- (3) Enables small amounts of colouring oxides to be introduced into a glaze which if brought in as the raw oxides would not be disseminated evenly in the whole mass of glaze.

Certain rules should be observed in fritting:

- (1) The ratio between acids and bases in the frit should be within the range of easy fusion, i.e. the acid molecules should not fall below the base molecules nor exceed them three times. The low limit is exemplified by the formula:



and the high limit by:



- (2) The two substances most commonly requiring fritting are the alkalis, nearly all salts of which are soluble, and boric acid which is itself soluble and also forms some soluble salts.

The alkalis are remarkable in that they form soluble silicates; therefore it is not enough to fuse a soluble alkali compound with silica, as this would not produce an insoluble silicate. For instance,  $K_2O \cdot 2SiO_2$  when fritted is soluble, but  $0.5K_2O \cdot 0.5CaO \cdot 2.0SiO_2$  is insoluble. A base which forms an insoluble silicate, e.g. lime, lead, zinc, alumina, etc., may reduce or inhibit the solubility of the alkaline silicates. Boric acid also requires crossing to make its products safe for use. A common practice years ago among some potters was to frit boric acid and flint together without any basic matter. Such a frit, however, is not insoluble.

A good rule to follow is to use at least two bases other than the alkalis, one of which shall be  $Al_2O_3$  if the glaze formula allows of this.

(3) The ratio between the alkalis and boric acid in the frit formula should be the same as in the completed glaze, otherwise some other source of alkali or  $B_2O_3$  will need to be introduced in the glaze, and to avoid this is the object of fritting.

(4) The ratio between the alkalis and the other elements of the frit must not fall below that existing in the glaze for the same reason as in (3). It may exceed this ratio, as additions of the insoluble bases are readily made in the glaze.

*Preparation of Frit.*—Any extra time spent on the preparation of and the thorough mixing of the ingredients of the frit is a very distinct advantage as usually the materials are purchased ready ground, and only need mixing in the desired proportions. The practice of mixing in a box by means of shovelling cannot be too strongly condemned. The method is inefficient and raises an injurious dust. A simple means of effecting efficient mixing is by means of a cylinder with paddle instead of pebbles, or a wooden barrel, preferably with an eccentric motion. A well-mixed frit should be readily fusible, and time is saved.

*Frit Kiln.*—The kiln in general use is of the type of the ordinary horizontal reverberatory furnace. The hearth of the furnace is composed of fireclay blocks and slopes to a central hole at the side. The fire gases coming from the grate pass over a firebridge, and thence over the hearth on which the charge has been filled through an opening in the top, and then passes on over another bridge at the end to the chimney.

The exit from the kiln is sealed with a fireclay block or a lump of china clay, and when the fused mass is ready for running off, this is withdrawn and the frit allowed to run into a tank of water placed underneath the opening. The water is then drained off and the frit taken to store ready to be ground with the other constituents of the glaze.

Where only small quantities of frit are required, such as frits for coloured glazes, the fusion may be conveniently carried out in a crucible furnace, many types of which are capable of being used either intermittently or continuously, the crucible being emptied into water as the frit is fused. Another method of making a small batch is by firing the crucible in the ordinary oven at the required temperature, but in this case the frit naturally sets to a hard

mass on the cooling of the oven, and is more difficult to break up for grinding.

\* In the typical glaze mentioned in the third group the lead is introduced in a raw state, viz., as white lead.

Some 40 years ago the Government appointed a commission to inquire into the prevalence of lead poisoning in the Potteries with a view to doing away with the use of lead in the glazes used. It quickly became recognised that it would be impossible to prohibit the use of lead compounds altogether, but suggestions for minimising the risks took the form of fritting the lead with other constituents of the glaze to render it insoluble in the gastric juices of the workers, and eventually the following restrictions were laid down as Special Rules by the Government ("Home Office Circular, December 14th 1889):

"No glaze into the composition of which lead or a compound of lead, other than galena, enters, shall be regarded as satisfying the requirement as to insolubility which yields to a dilute solution of hydrochloric acid more than 4% of dry weight of a soluble lead compound calculated as lead monoxide when determined in the following manner: 'A weighed quantity of dried material is to be continuously shaken for one hour, at the common temperature, with 1,000 times its weight of an aqueous solution of hydrochloric acid containing 0.25 of HCl. This solution is thereafter to be allowed to stand for one hour, and to be passed through a filter. The lead salt in an aliquot portion of the clear filtrate is then to be precipitated and weighed as lead sulphate.'"

The general results of the application of these regulations to the pottery industry during the last 30 or 40 years has been the practical elimination of the grave risk of plumbism amongst the operatives.

While the general rule laid down seemed to be simple, many factors in the method of preparing the lead frits exert their influence on the final solubility of the product.

T. E. Thorpe in his evidence to the Lead Commission stated that "the insolubility of the lead depends not upon any one oxide or group of oxides with which it may be associated, but upon the maintenance of a certain ratio between the whole of the basic oxides on the one hand and the whole of the acidic oxides on the other; the acidic oxides in this case being silica and boric oxide." Thorpe therefore proposed an empirical rule which gives a very fair indication of the "low solubility" of a frit or glaze.

The rule may be stated thus:

$$\frac{\text{Sum of bases (including } Al_2O_3) \times 223}{\text{Sum of acids (including } B_2O_3) \times 60} = 2\frac{1}{2} \text{ or less,}$$

where 223 is the molecular weight of  $PbO$  and 60 the molecular weight of  $SiO_2$ .

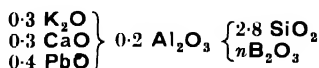
In taking this rule as a guide for compounding a lead frit, however, certain factors must be considered which are likely to affect the solubility:

(1) The proportion of  $B_2O_3$  to  $SiO_2$ , for if the former is unduly high, the frit produced will not conform to the Government test, although

Thorpe's ratio gives a figure below the calculated limit of solubility.

The effect of  $B_2O_3$  on the solubility of a lead frit is illustrated as follows, by the work of G. D. Horley (Trans. Ceram. Soc. 1935, **34**, 166):

Frit composition

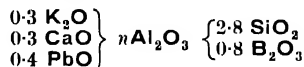


boric oxide being the only variable

$n$	0	0.1	0.5	0.8
PbO solubility	0.19	0.91	1.07	5.80%

while the effect of alumina in counteracting the deleterious effect of boric oxide is shown in the following tests by the same investigator:

Frit composition:



where alumina is the only variable

$n$	3	0	0.05	0.15	0.30
PbO solubility	11.38	9.64	5.56	5.46	%

Another suggestion to overcome the action of increased solubility is the substitution of boracite or colemanite (both insoluble calcium borates) as the source of  $B_2O_3$ .

(2) Another factor affecting the solubility of a lead frit is the fineness of grinding. W. Jackson and E. M. Rich (Mem. Manchester Phil. Soc. 1900, **45**, No. 2) showed that the solubility of a frit varies with its degree of fineness. Their results obtained on elutriation in Schöne's apparatus gave:

Gauge reading	1	5	50	100	cm.
Solubility	17.5	8.7	4.0	1.5%	PbO

While then it is evident that the fineness of subdivision has an influence on the degree of solubility, the effect is too small to be of serious moment within the limits of fineness occurring in actual practice.

The observations on the solubility of lead frits are important, but it must be remembered that the Government restrictions are applicable to the glaze as a whole and not to the lead frit contained in it. The amount of lead frit in a standard glaze rarely exceeds one-third of the whole, and it is quite possible that while the lead frit itself would not conform to the Thorpe ratio, the glaze as a whole might be well within the limits of the Government requirements, the remaining two-thirds of the glaze mixture being composed of entirely insoluble material.

In practice, it is usual to adopt the bisilicate of lead or even more complex silicates in order to keep the solubility as low as possible, and the preparation of low-solubility glazes was considerably simplified by the introduction of lead silicates of a definite composition by the sup-

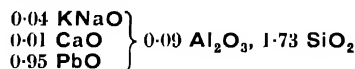
pliers, the most general being the so-called bisilicate of lead.

A word of caution should, however, be given to those changing from a raw lead to a fritted lead glaze. The composition of a bisilicate of lead ( $PbO, 2SiO_2$ ) is approximately PbO 65 and  $SiO_2$  35%, but a typical analysis of the market product shows that, while being of a composition tending to keep the solubility at a low figure, it can hardly be considered as a true bisilicate and, unless allowance is made for the other ingredients introduced, the final result of the glaze may be disappointing.

Analysis of commercial bisilicate of lead:

$SiO_2$	31.60
$Al_2O_3$	2.73
$Fe_2O_3$	0.11
MgO	0.11
CaO	0.04
$K_2O$	0.28
$Na_2O$	0.62
PbO	64.30
Loss on ignition	0.20
	<hr/> 99.99 <hr/>

with approximate formula:

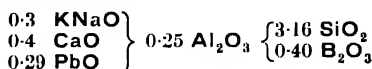


The change in composition from a glaze, containing raw lead compounds, to one of fritted lead for a good class earthenware body is indicated in the following example from actual experience.

The analysis of the original glaze gave:

$SiO_2$	51.40
$Al_2O_3$	6.05
CaO	6.20
$K_2O$	1.90
$Na_2O$	3.92
PbO	17.50
$B_2O_3$	8.06
Loss on ignition	3.90

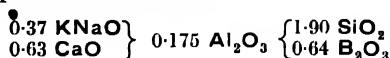
Approximate formula:



The recipe:

Frit		Glaze	
Borax	38.0	Frit	37.0
Whiting	19.0	White lead	21.0
Cornish stone	19.0	Cornish stone	32.0
Flint	19.0	Flint	10.0
China clay	5.0		
	<hr/> 100.0 <hr/>		<hr/> 100.0 <hr/>

Approximate formula of frit:



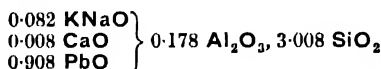
The low-solubility glaze was made up from :

Borax frit (as above)	44.5
Lead frit <sup>1</sup>	30.0
Cornish stone	25.0
Flint	0.5

100.0

This change gave practically the same chemical formula and at the same time brought the glaze well within the Home Office requirements, while the appearance and durability were not affected.

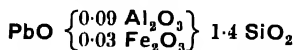
Another very popular composition for a lead frit and largely used by potters making their own frits is red lead 50, Cornish stone (china stone) 25, flint 25 parts with approximate formula :



Such a frit is found in practice to be more insoluble than the previously mentioned bisilicate.

**Lead Glazes.**—The great variety of pottery bodies made from such different clays and admixtures necessitates such a range of glazes, that to set a standard to suit all requirements would be impossible. The numerous published recipes, however, when calculated out to the suggested formula, can be reduced to a few main types which may be classified according to their lead content.

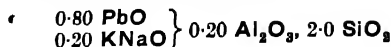
**Red Ware.**—This is the simplest and cheapest type of glazed pottery formed often from natural clay alone, such as is used for common bricks, but washed before use. Such clays are fired at relatively low temperature, approximately 900°C. The products in this grade consist of such articles as milk crocks, common bowls, teapots, etc. The glaze for such bodies is of the basic type and is often applied on the clay ware; it sometimes consists solely of a wash of litharge or galena, and depends on the adsorption of sufficient alumina and silica from the body during firing to form the glaze. An approximate formula of such glaze after firing is :



Naturally, such a basic glaze is very liable to the action of acids and not to be recommended for use on vessels intended for domestic purposes.

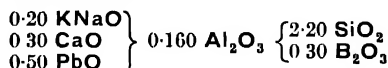
A higher grade of Red Ware is that known as "Rockingham" which consists of better class red clays and often mixed with a proportion of ball clay or china clay and flint, the desired tone of colour being given by the addition of ochre. This class of body is usually given a biscuit fire at approximately 1,100°C. before being glazed, although at the present time considerable quantities are being completed in one fire only. The glaze for this class is usually of the raw-lead type consisting of white lead, Cornish stone, china clay and, flint, to which is added manganese dioxide.

An approximate formula is :



with approximately 10%  $\text{MnO}_2$  added.

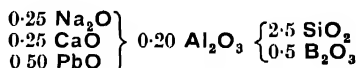
Closely allied to the Rockingham grade is the one known as "Jet Glaze." This is applied to the same red body as used for Rockingham, but to give the jet-black coloured glaze, cobalt oxide is substituted for the manganese dioxide used in the Rockingham glaze. During the last few years considerable progress has been made with a view to substituting glazes of a low-solubility nature for this grade of ware in order to be free from the restrictions imposed on users of raw-lead glazes. One such low-solubility glaze approximates to the formula :



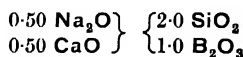
with the addition of 10%  $\text{MnO}_2$  and compounded from borax frit, lead frit, Cornish stone, china clay and manganese dioxide.

Another type of high-lead glaze, formerly extensively used, is that termed "Majolica Glaze." This grade of earthenware was in great demand years ago in the manufacture of ornamental goods such as flower pots, umbrella stands, pedestals, etc., the body being made from a cheap earthenware recipe, fired biscuit at a relatively low temperature and covered with a soft glaze often made up by the addition of colouring oxides to a standard white glaze.

A typical glaze of this type would correspond to the formula :



prepared from a frit of the formula :



with the addition of white lead, china clay and flint. The colouring agent would then be added in the desired proportion during the grinding of the glaze.

As will be seen from the formulae, the foregoing four types of glaze are all of high lead-content, approximating to between 40 and 50%  $\text{PbO}$ , but are used on common clay bodies of uncertain colour! Lead glazes are also used for what are termed "white-ware bodies" and these cover a wide range from the common earthenware to the highest class semi-porcelain and china.

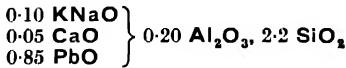
While the materials used in the various bodies are practically the same for all types, the proportions and qualities vary widely; a few typical examples will furnish a fair idea of the general range.

**Common Earthenware**, formerly designated by the term C.C. or cream colour. Here the body is usually composed of the cheaper varieties of china and ball clays with the addition of Cornish stone and flint. The clay content is usually higher than in better-class wares, to ensure easy

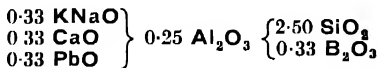
<sup>1</sup> Commercial bisilicate.



working properties, and the fineness of texture, etc., required do not demand so much preparation of the clay body. The percentage composition of a typical cream-colour body is ball clay 34, china clay 26, flint 25 and Cornish stone 15, but the glaze used is practically the same in both cases. A simple glaze largely used for this type before the introduction of the low-solubility variety had the recipe, white lead 59.0, Cornish stone 31.7 and flint 9.3 parts, corresponding to the formula :



but since the introduction of fritted glazes a more general formula has been :



made up from a borax frit with Cornish stone, china clay and white lead added.

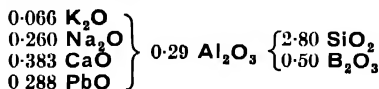
The bodies for the higher grade of earthenware and semi-porcelain and the type formerly known as "Granite" are usually compounded from better class clays and Cornish stone; the clay content is lower and the flint and stone content higher, thus giving a better colour and increased vitreousness. A body of this type will approximate to the recipe, ball clay 30, china clay 20, flint 33 and Cornish stone 17%, and to give extra whiteness a small proportion of cobalt oxide stain is added, approximately 1 in 12,000 parts. The working clay is prepared with extreme care to ensure as clean a body as possible.

The body of china is distinguishable from earthenware by reason of its translucence, and is compounded from calcined bone, Cornish stone and china clay with the addition of a small quantity of ball clay to increase plasticity, although this detracts somewhat from the perfect colour.

A typical bone-china body has the following percentage composition : bone 46, Cornish stone 29, china clay 23 and ball clay 2, varying slightly according to quality required.

The glaze usually adopted for both the better class earthenware and the china is now the low-solubility type composed of borax frit, lead frit and mill mixture, being mainly Cornish stone, flint and china clay.

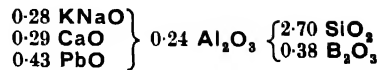
A typical formula would be :



Such glazes represent a lead content of approximately 18% PbO.

Other white-ware glazes in which lead is used are those for white tiles, in which the body contains a very high proportion of flint, sometimes as high as 45% owing to the necessity of freedom from warping during firing. The glaze for such bodies is usually much higher in lead content than the other white-ware bodies, varying from 25 to 40% PbO.

A typical formula is :



maturing at a temperature of 970°C., compounded from borax frit, Cornish stone, china clay and white lead.

**Leadless Glazes.**—The restrictions on the use of lead have led to much research to find a satisfactory glaze entirely free from that substance, with the result that many lead-free glazes are now in use; these, while giving very good results, do not quite reach the brilliance obtained when using lead; nor is the palette of the decorator so unlimited, as many colours are affected both in tint and brilliance by the absence of lead.

One of the first such *leadless glazes* used some 50 years ago was composed of a frit as follows :

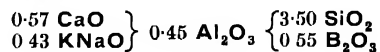
Felspar . . . . .	47.0
Borax . . . . .	30.0
Sand . . . . .	6.5
China clay . . . . .	5.5
Nitre . . . . .	5.5
Soda ash . . . . .	5.5

5% calcined borax added during grinding.

Corresponds to formula :



Such a glaze was found to have a marked effect on the colours used in decoration, and owing to high content of  $\text{B}_2\text{O}_3$ , and to being all fritted, difficulty was experienced in keeping the glaze in suspension during the dipping process. At the present time, the practice conforms to the use of a glaze approximating to the formula :



compounded from a frit consisting of :

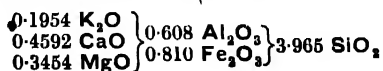
Borax . . . . .	27.0
Flint . . . . .	20.0
Whiting . . . . .	12.0
Felspar . . . . .	22.5
China clay . . . . .	18.5

with 2½% china clay added during grinding.

Such a glaze in practice gives a very satisfactory result.

Other leadless glazes, apart from those covered by the first class, are those termed :

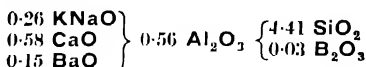
**Slip Glazes.**—These are mainly used in connection with once-fired stoneware; in some cases they may be simply a very fusible clay giving of itself a good even glaze when fired. The best example of such a clay glaze is the one known as "*Albany Slip*," largely used in the United States and having the formula :



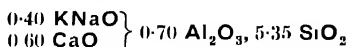
giving when fired to approximately 1,250°C. a dark dark brown colour.

The colour is, however, a drawback for some purposes, and to meet the demand for a cleaner looking lining for the ware, potters resort to a whitish semi-opaque glaze composed of felspar or Cornish stone, whiting and flint with sometimes a little barytes and, if required, softened by a small proportion of a soft frit.

Such a glaze taken from practice has the following formula :



A very simple slip glaze may be compounded from Cornish stone 75, felspar 15 and whiting 10% and maturing at approximately 1,250°C., giving the formula :



**Coloured Glazes.**—This term is mainly used to describe those bodies covered entirely with a glaze in which is incorporated a certain proportion of a colouring oxide, and does not refer to the colouring obtained by the use of a printed or painted decoration on the biscuit ware.

Such glazes are usually confined to majolica ware and to tiles, but sometimes they are also used in stoneware. In the case of majolica and tiles, it is essential that the firing temperature be relatively low, approximately 960°C., consequently the lead content is high. To give the necessary colour, it is usual to grind a percentage of colouring oxide with a portion of the glaze and then mix well with the whole batch. A more satisfactory method, however, is to use (1) a batch of transparent glaze, (2) a batch of coloured glaze too high in colouring oxide for the purpose required. By using suitable proportions of each, any desired blend can be obtained. Much time is saved by adopting this method and the inconvenience of storing a large number of blends is avoided. A simple example will illustrate the procedure :

Transparent glaze No. 1, formula 1.00 PbO: 0.15 Al<sub>2</sub>O<sub>3</sub>, 1.75 SiO<sub>2</sub>, and with this as base a series of majolica glazes are to be made with cobalt oxide as colouring agent.

For this purpose a glaze No. 2 is made up, having the formula :

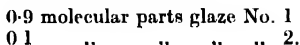


This glaze will be black in colour and can be used with No. 1 in any desired proportion.

If glaze No. 3 is required to contain 0.02 mol. parts of CoO, the difference between the CoO content of glaze No. 2 and the required CoO content of glaze No. 3 is 0.18 mol. parts. Dividing the difference in the CoO content of the desired glaze and one extreme by the total difference between the two extremes gives a fraction expressing the proportion of the opposite extreme to be used in the mixture, thus :

$$\frac{\text{Desired difference}}{\text{Total difference}} = \frac{0.18}{0.20} = 0.9$$

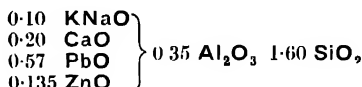
Therefore glaze No. 3 requires :



This method has the advantage that the glazes Nos. 1 and 2 can be kept in the slop state and thus readily mixed without the necessity of drying; the only precaution being that the dry content per unit volume of the slop glazes be known.

A more perfect mixture is, however, obtained if the colouring oxide in glaze No. 2 is embodied in a fritted form.

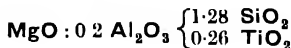
**Matt Glazes.**—Of recent years, such glazes have received much attention owing to their decorative possibilities and are largely used in the tile and ornamental trades. Many of these glazes are compounded by the addition to a transparent glaze of a so-called matt mixture, depending for its composition on the type and colour of the surface required. The matt effect is produced by the addition of either alumina, lime or magnesia, with the addition of zinc oxide to give the desired sheen. These glazes may also be made direct as raw glazes. A typical raw matt-glaze has the composition: red lead 42.0, whiting 6.4, felspar 16.0, china clay 21.5, flint 10.6 and zinc oxide 3.5%, corresponding to the formula :



and matures at 1,080°C.

Many examples of such glazes are quoted by C. F. Binns (Trans. Amer. Ceram. Soc. 1903, 5, 50).

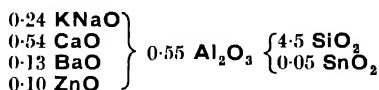
A type of lime matt-glaze is produced by the addition of approximately 25% whiting to an ordinary low-solubility transparent glaze. Coloured matt-glazes may be produced by using any of the usual coloured glazes with the addition of a matt mixture, this being either added to the transparent glaze or sometimes dipped on the top of the glazed piece before firing. One such matt mixture used in practice has the percentage composition : SiO<sub>2</sub> 36.97, Al<sub>2</sub>O<sub>3</sub> 9.36, TiO<sub>2</sub> 9.90, MgO 19.27 and CO<sub>2</sub> 23.47, corresponding to the formula :



Care must be taken in the selection of a suitable matt mixture as this will exercise considerable influence on the final colour. As an instance, if the above matt mixture be superimposed on a blue glaze, the resultant colour instead of being a matt blue will be of a dark plum colour, owing to the action of the magnesia on the cobalt oxide in the base glaze.

**Fireclay Glazes.**—The usual colour of fireclay when fired is a deep buff, and if glazed with a transparent glaze the same colour is naturally apparent. In such cases as cheap cane sanitary-ware, this colour is not considered detrimental, but in the case of better-class ware, the trade demands a white appearance. This effect can

be produced on the buff coloured body by the use of an *engobe*, which is an intermediary between body and glaze and is usually made by mixing part of the buff body with a proportion of a white-burning clay. In the higher class of fireclay sanitary-ware, it is necessary to have several coats of the engobe to mask thoroughly the colour of the body, and each succeeding coat should have a higher proportion of the white body, thus gradually correcting any differences in the contraction of the original body and that of the white engobe. The composition of the white engobe usually approximates to that of an ordinary earthenware body. The glaze then applied on the engobe will approximate to formula :



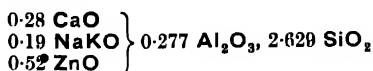
and will mature at about 1,250°C.

A similar procedure will be followed in the production of glazed bricks with possibly the addition of colouring oxides as required.

The composition of the glaze will, of course, depend on that of the body and this will vary according to the grade of the fireclay used, but the quoted example is one taken from practice and used on a second-class fireclay and gives a fair indication of the composition of such glazes.

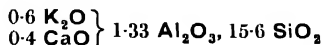
**Decorative Glazes.**—Many varieties of glaze are used for the purpose of decoration. The beautiful effects of many of the art potteries and also of the studio potters are examples of what can be done by the blending of coloured glazes in producing pleasing effects. Such glazes are usually of the majolica type, and the effects are produced by superimposing one glaze on the other before firing, as instanced by dipping a turquoise glaze on the top of a blue one. Mottling can also be introduced with good effect by dabbing one colour with a sponge on the ware and then dipping the piece in a glaze of another colour.

From an academic standpoint, the outstanding example of a decorative glaze is the one known as crystalline glaze. The application to ceramics of super-saturation, so usual in pure chemistry, has long exerted a fascination on ceramic chemists whose object was to introduce substances into the glaze which, during the cooling process, would separate out as crystals. Up to the present time zinc oxide has been found to give the most satisfactory results in the production of crystals of zinc silicate. Various colouring oxides can be added in small proportions to enhance the effect of the crystallisation. The earliest work on the subject was done by Lauth and Dutailly and reported in their work "La Manufacture Nationale de Sèvres," 1879-87; Paris, Librairie I. B. Bailliere et Fils, 1889, in which they give the following recipe for producing the best crystals when fired to a temperature of 1,350°C. :  $\text{SiO}_2$  57.49,  $\text{Al}_2\text{O}_3$  11.68,  $\text{CaO}$  6.72,  $\text{NaKO}$  6.12 and  $\text{ZnO}$  18.00%, corresponding to the formula :

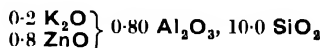


Outstanding pieces of these productions are to be seen in the showrooms of the Royal Works at Sèvres.

The Royal Copenhagen factory has also specialised in crystalline glazes, but their results are obtained by two fires. The first glaze is of the hard porcelain type, approximating to the formula :



maturing at approximately 1,450°C., and on this a softer glaze high in zinc oxide is applied having the formula :



and fired to approximately 1,350°C.

Softer crystalline glazes can be compounded by the substitution of boric acid for part of the silica.

A simple low temperature glaze maturing at 1,150°C. has the following recipe : leadless glaze 100, zinc oxide 20, rutile 10 and cobalt oxide 1 part, of formula :



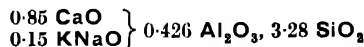
Many other examples of such glazes are included in a paper by Purdy and Krehbiel (J. Amer. Ceram. Soc. 1907, 9, 319).

**Crackled Glazes.**—One of the chief defects of glazes, viz., crazing, has been utilised, originally by the Chinese and Japanese potters, as a means of decoration under the term "Craquelé." This effect has also been developed in the researches of Lauth and Dutailly (Bull. Soc. chim. 1888, [ii], 49, 948) who found that by modifying the composition of an ordinary stable glaze, by increasing the silica and alkali content and decreasing the lime and alumina, very handsome cracked glazes can be produced on soft porcelain, and they give the following recipes :

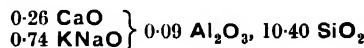
	Ordinary glaze.	Crackled glaze.	
		No. 1.	No. 2.
$\text{SiO}_2$ . . .	66.18	79.42	69.92
$\text{Al}_2\text{O}_3$ . . .	14.55	11.89	18.13
$\text{CaO}$ . . .	15.90	2.88	—
Alkalis . . .	3.55	5.81	11.90

corresponding to the formula :

Ordinary glaze :



Crackled No. 1 :



Crackled No. 2 :



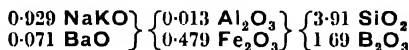
The temperature required for the firing of the crackled glaze is higher than the ordinary glaze. Some very pretty effects are produced by filling up the fine cracks (crazes) with a very fusible coloured frit and firing again at a low temperature.

**Aventurine Glaze.**—This is another example of a type of crystals produced at a low temperature, approximately 960°C., showing, when properly matured, golden spangles or crystals in a red ground. Usually the best results are obtained in glazes free from lead and with about 25% of iron oxide, of which a great part separates out in a crystalline state on cooling. Anon., *Sprechsaal*, 1906, 89, 264, gives the following recipe :

*Frit*

Sand . . . . .	444
Borax . . . . .	330
Ferric oxide . . . . .	148
Felspar . . . . .	14
Potassium nitrate . . . . .	38
Barium carbonate . . . . .	27

corresponding to the formula :



Oxidising conditions are essential to produce the desired result.

**Red Glaze.**—A good red glaze without crystals can be produced from the above recipe, by the addition of 33½% bisilicate of lead and firing to a temperature of 1,100°C.

**Rouge Flambé, Chinese Red or Sang de Bœuf.**—This glaze, originally the work of the Chinese, has been the subject of much research work, mainly by Lauth and Dutailly (*Bull. Soc. Chim.* 1888, [ii], 49, 591) and Seger ("Seger's Collected Works," 1902, II, 708).

The colouring agent is undoubtedly copper, but the results obtained are due to the nature of the glaze and its mixing and application, and more especially to the method of firing.

An analysis of a piece of glaze from a Chinese vase gave the following results:  $\text{SiO}_2$  73.90,  $\text{Al}_2\text{O}_3$  6.00,  $\text{Fe}_2\text{O}_3$  2.10,  $\text{CaO}$  7.30,  $\text{K}_2\text{O}$  3.00,  $\text{Na}_2\text{O}$  3.10 and  $\text{CuO}$  4.60%.

A glaze made up from this recipe and applied to a porcelain body and fired in a reducing fire in a special kiln gave the first satisfactory results produced in Europe. The great difficulties attending the production of the true Chinese Flambé have led to many attempts to simplify the method, and a very popular one is that of coating the already glazed piece with a mixture of china clay and copper carbonate or acetate and firing at a low temperature, approximately 800°C., in a reducing atmosphere; on drawing from kiln, the clay is washed off, leaving the original glaze impregnated with a deposit of copper and, if properly compounded and fired, giving a rich Sang de Bœuf effect.

**Defects of Glazes.**—The two principal defects to which glazes on pottery are subject are (1) "crazing" and (2) "peeling."

Crazing is the defect appearing on the surface of the ware in the form of a network of fine cracks, while peeling takes the form of the glaze

"chipping" or "scaling" off the surface of the ware, usually at the edges.

• Broadly speaking, both faults are attributed to the same cause, viz., a difference in the coefficients of expansion of the body and the glaze. If the glaze, during cooling, contracts more than the body, strains are set up and crazing will result, while if the glaze during cooling contracts less than the body, the glaze peels or scales off. Such statement appears on the face very simple, but there are so many other factors to be considered that those interested in the subject should consult the voluminous survey of the literature up to 1934 compiled by J. W. Mellor (*Trans. Ceram. Soc.* 1935, 34, 1-112) as well as recent work on various aspects of crazing by H. W. Webb (*ibid.* 1939, 38, 75) and F. T. Wood and S. R. Hind (*ibid.* 1939, 38, 435).

While the actual principles involved are still the subject of much discussion, the practical potter has at hand ready means of controlling the fault. The usual remedy adopted to prevent crazing is to increase the silica content of the body, while to remedy peeling, the lowering of the silica content is the method adopted. The altering of the body is usually preferred to any interference with the glaze, as it is inferred that the body materials are more liable to fluctuation than those of the glaze. If, however, the latter be adopted, the silica content of the glaze must be raised to lower the tendency to crazing, while to remedy peeling the silica content must be reduced.

Seger, whose pioneer work on the subject has been the main guide for succeeding workers, formulated a series of rules which, while not universally applicable to all conditions existing in pottery bodies, forms a very serviceable basis on which to work, but as mentioned above, the practical potter does not concern himself much with the academic issue involved while he has a ready and simple means of overcoming the trouble.

Full details of Seger's Rules may be found in "Seger's Collected Works," 1902, II, 567, 581.

**Enamels.**—This term is usually applied to glasses rendered opaque by the addition of colouring oxides, but in ceramics is understood to mean soft glazes with which are incorporated colouring oxides and applied to the ware in what is known as "on glaze" decoration, and therefore commonly called "enamel colours."

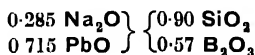
These colours consist of colour base and flux. The colour base may be metallic oxides alone or silicates, borates or aluminates of the metals. In some cases the colour base and flux are simply ground together while in other cases they are ritted together, thus ensuring a perfectly uniform product. The maturing temperature for enamel colours varies between 760° and 850°C. The composition of the flux must necessarily be considered in its relation to the oxide used and also to the nature of the glaze as the final colour produced will depend on agreement of the two, so that the composition of fluxes varies very widely.

Three essential properties of the finished colour are :

- (1) Must adhere strongly to the glaze.
- (2) Must be fusible enough to penetrate to the desired depth.

(3) Must have a correct coefficient of expansion to prevent scaling or peeling.

The commonest flux used in this country is known as No. 8 flux and is made by fritting, at approximately 900°C., red lead 30, borax 20 and flint 10 parts, corresponding to the formula :



A typical recipe is as follows :

**White Enamel.**—Tin oxide 20, felspar 10 and No. 8 flux 20 parts, ground together.

Coloured enamels may be produced by the addition to the flux of the various oxides thus : cobalt for blues ; chromium or copper for greens ; manganese for browns ; antimony or uranium for yellows ; iron for reds ; and iridium or a mixture of cobalt and manganese for black.

**Under-Glaze Colours.**—These colours are used on what is termed biscuit ware and are developed by the covering glaze during firing. The colour itself will be influenced by :

- (1) The temperature of the kiln.
- (2) The atmosphere of the kiln.
- (3) To some extent by the composition of the body.
- (4) The composition of the glaze.

The high temperature necessary to fuse the glaze naturally limits to some extent the variety of colours used for under-glaze decoration.

The general colours in use are blue, black, brown, green, yellow and pink, and are made up from colouring oxides with the addition of fluxing material.

A typical recipe is : **Blue.**—Cobalt oxide 1, zinc oxide 4 and flint 2 parts, calcined at approximately 1,250°C. and finely ground. Any desired shade may be obtained by the addition of flux consisting of approximately : flint 12, Cornish stone 12, whiting 5 and borax 4 parts, fritted at 1,000°C.

**Blacks** are usually prepared from mixtures of iron, chrome and cobalt, and a typical recipe is :  $\text{Fe}_2\text{O}_3$  80,  $\text{Cr}_2\text{O}_3$  76.2 and  $\text{Co}_2\text{O}_3$  10 parts, fritted at 1,250°C.

**Greens** are obtained from chromium or copper oxides ;

**Pinks** from tin oxide, whiting and potassium dichromate ;

**Browns** from manganese and mixtures of manganese and chromium oxides ;

**Yellow** from uranium and antimony oxides.

A. H.

**GLESSITE** (v. Vol. I, 302d).

**GLIADIN** (v. Vol. II, 85a).

**GLIMMERTON** (v. Vol. III, 196c).

**"GLOBLAK"** (v. Vol. II, 480a).

**GLOBULINS.** General term for proteins which are coagulated by heat, are insoluble in water but dissolve in dilute solutions of neutral salts, acids and alkalis. They are precipitated in half-saturated ammonium sulphate or in fully saturated sodium chloride or magnesium sulphate solutions.

**GLOBULOL.** The sesquiterpene alcohol, *globulol*, b.p. 283°/755 mm.,  $[\alpha]_D -35.29^\circ$ , occurs in the essential oil from the leaves of *Eucalyptus globulus* (Schimmel's Report, 1904, 1, 46; Semmler and Tobias, Ber. 1913, 46, 2030;

Ruzicka, Pontalti and Balas, Helv. Chim. Acta, 1923, 6, 861). On dehydrogenation it yields cadalene (q.v.) but its structure has not been determined.

J. L. S.

**GLONONIN (E OIL** (v. Vol. IV, 491d).

**GLORIOSINE** (v. Vol. III, 276c).

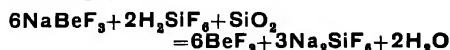
**GLUCAL** (v. Vol. II, 294c).

**GLUCINUM** (*Beryllium*). Be. At. no. 4. At. wt. 9.02. Two isotopes (8), 9. This fourth member of the atomic series was first detected in beryl by L. N. Vauquelin (Ann. Chim. Phys. 1798, [i], 26, 155), and from this source he isolated the oxide "la terre du beril" and prepared some of its salts ; in a footnote (l.c. 169) the editors of the Annales proposed the name glucine for the oxide on account of the alleged sweet taste of the salts. The metal was not isolated until 30 years later when Wöhler obtained it by heating the chloride with potassium. He called it *beryllium*, the name by which it is best known, and which will be adopted throughout this article. The name still used in France is glucinium.

There are several beryllium minerals, such as euclase,  $\text{Be}(\text{AlOH})\text{SiO}_4$  ; phenakite,  $\text{Be}_3\text{SiO}_4$  ; chrysoberyl,  $\text{BeAl}_2\text{O}_4$  ; beryllonite,  $\text{NaBePO}_4$  ; and hambergite,  $\text{Be}_2(\text{OH})\text{BO}_3$  ; but beryl,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , is still the only practical source of the metal although its refractory nature has led to much effort in devising suitable methods for its decomposition. Usually some modification of Copaux's method is adopted (Compt. rend. 1919, 168, 610) in which the finely ground mineral is fused with sodium silicofluoride at about 700–800°C. Aluminium and magnesium form insoluble fluorides, ferric iron is unattacked while the soluble double fluoride,  $\text{NaBeF}_3$ , is extracted with water. Air is blown through the solution to oxidise any ferrous iron, which is then removed, and the filtrate is evaporated to yield crystals of the double fluoride. From this product pure beryllium compounds may be obtained by one of the following methods :—

(a) A solution of the double salt is treated with a slight excess of lime and the precipitate of  $\text{CaF}_2$ ,  $\text{Be}(\text{OH})_2$  and excess  $\text{Ca}(\text{OH})_2$  is extracted with hydrofluoric acid ; evaporation of the filtrate at 100° yields the hydrated fluoride or basic fluorides which, when heated to 300°, produce the oxyfluoride,  $2\text{BeO} \cdot 5\text{BeF}_3$  (Illig *et al.*, Wiss. Veröffentl. Siemens-Konzern, 1929, 8, [i], 34).

(b) The double salt solution is allowed to react with silica and silicofluoric acid according to the equation



After removing the insoluble sodium silicofluoride the filtrate is worked up as in (a) (see also Gadeau, Rév. Met. 1935, 32, 627, and F.P. 742619).

(c) The double fluoride is converted to sulphate by heating with conc. sulphuric acid, any alkaline earth sulphate being removed and the filtrate oxidised with hydrogen peroxide. A quarter of the resulting solution is treated with ammonia, the crude beryllium hydroxide filtered off and a part of it added to the re-

maining solution thereby causing precipitation of much of the impurity. The process is repeated and the final filtrate acted on with hydrogen sulphide to remove traces of the heavy metals. Dilution of the solution with 8-8.5 times its volume of water induces precipitation of the hydroxide; the basic sulphate (about 10%  $\text{SO}_3$ ) which it contains is decomposed by heating with carbon black at  $700^\circ$  (Sloman, J.S.C.I. 1929, 48, 309r).

More recently it has been found that beryll which has been heated to its melting-point and then quenched in water is easily attacked by strong sulphuric acid. The solution of beryllium, aluminium and alkali sulphates is then concentrated, the removal of aluminium being facilitated by adding ammonium sulphate so that an alum crystallises out. The resulting beryllium sulphate is decomposed to the oxide at  $1,450^\circ$  (Sawyer and Kjellgren, Ind. Eng. Chem. 1938, 30, 501).

**PREPARATION OF THE METAL.**—Large-scale production of the metal is carried out by electrolysis of fused salts, a procedure which was first successfully employed by Lebeau (Compt. rend. 1898, 126, 744) who electrolysed a fused mixture of sodium and beryllium fluorides at  $300^\circ$  in a nickel crucible which served as the cathode and upon which the metal was deposited in flakes. For coherent deposits the bath temperature must exceed the melting point of beryllium and in order to achieve this barium fluoride is added; even so there is always a notable volatilisation of beryllium fluoride. Usually a graphite pot is employed with graphite anodes, the cathode being a water-cooled iron or steel rod tipped with beryllium (Stoek and Goldschmidt, G.P. 375824; B.P. 192970; Vivian, Trans. Faraday Soc. 1926, 22, 211). Later work has shown that it is preferable to use mixtures of beryllium oxyfluoride with sodium or barium fluoride. The process is made continuous by adding oxyfluoride from time to time; volatilised salts are recovered by means of absorption towers (G.P. 467247; B.P. 278723).

Fused mixtures of beryllium and alkali chlorides have also been electrolysed at temperatures between  $370$  and  $400^\circ\text{C}$ . The metal separates as spangles which are rendered coherent by pressing into rods and melting under fused barium chloride (B.P. 377858, 434338).

Beryllium produced electrolytically is contaminated with oxide, nitride and carbide; a surface skin of the last-named is always noticeable but may be removed by dipping the metal in molten sodium hydroxide. Impurities may also be got rid of by melting the crude metal either *in vacuo* in a high-frequency induction furnace or under a mixture of alkali and alkaline-earth halides when the dross sinks to the bottom. Further purification can be achieved by subliming the metal in a high vacuum (Vivian, *loc. cit.*; G.P. 443944, 465525; Sloman, J. Inst. Metals, 1932, 49, 365; Losana, Alluminio, 1939, 8, 67).

**NUCLEAR REACTIONS.**—Beryllium is apparently a simple element in that the mass spectrograph fails to reveal any lines other than that corresponding to a mass of 9; nevertheless, the isotope of mass 8 has been frequently postulated in transmutation reactions. Thus

Laaff (Ann. Physik, 1938 [v], 32, 743) states that the  $^9\text{Be}$  nucleus is produced in the process  $^{11}\text{B}(p, \alpha)^9\text{Be}$  but that it disintegrates into two  $\alpha$ -particles. On the other hand Gluckauf and Paneth (Proc. Roy. Soc. 1938, A, 165, 229) irradiated  $^9\text{Be}$  with  $\gamma$ -rays from radon and from the quantity of helium produced they concluded that the reaction produced two  $\alpha$ -particles and a neutron in preference to  $^9\text{Be}$  and a neutron. By this transformation is most probably produced the helium which is often found in beryll and in amounts related to the age of the mineral (Rayleigh, *ibid.* 1933, A, 142, 370; Burks *et al.*, Compt. rend. Acad. Sci. U.R.S.S. 1937, 15, 193). The mass difference of  $^9\text{Be}$  and  $^8\text{Be}$  is 1.0072 while the stability of  $^9\text{Be}$  with respect to two  $\alpha$ -particles is given as 0.3 m.e.v. (Allison *et al.*, Physical Rev. 1939, [2], 55, 107, 624; Collins *et al.*, *ibid.* 172).

**PHYSICAL PROPERTIES.**—Beryllium is a hard, brittle, steel-grey metal possessing a low sp.gr. ( $1.84$  at  $20^\circ$ ) and high melting-point ( $1,285^\circ\text{C}$ ). It crystallises in hexagonal plates, the crystal lattice being a hexagonal close pack with lattice constants,  $a = 2.268$ ,  $c = 3.594$ , axial ratio 1.585. The work of Jaeger and his collaborators indicates that beryllium exhibits allotropy, a metastable form at  $600^\circ$  being interesting in possessing a super-lattice containing some 60 atoms. Although normally brittle the metal does acquire some ductility on heating while, according to Sloman, pure beryllium is ductile at room temperature. Other physical properties are tabulated below:

*Atomic volume*, 5.

*Hardness*, 130 Brinell for 99.8-99.9% metal and 60-65 for 99.9%.

*Young's modulus of elasticity*, 30,000 kg./sq. mm., a calculated value (Schwerber Metallborse, 1928, 18, 706).

*Vapour pressure*, 5 mm. at  $1,530^\circ\text{C}$ , 760 mm. at approximately  $3,040^\circ$ .

*Heat of fusion*, 345.5 g.-cal.

*Heat conductivity*, 0.3847 at  $0^\circ$  and increases regularly with temperature as expressed by the equation  $K = 0.3847 + 0.00751t - 0.000468t^2$ .

*Specific heat*. Presumably as a result of allotropic modification this property varies with the thermal treatment accorded to the metal. Constant values are said to be given by powdered beryllium (Jaeger and Rosenbohm, Rec. trav. chim. 1934, 34, 451; Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 67).

*Linear coefficient of expansion*, ( $20$ - $100^\circ\text{C}$ .)  $12.3 \times 10^{-6}$ ; ( $20$ - $300^\circ\text{C}$ .),  $14.0 \times 10^{-6}$ .

*Specific resistance*. Like many of the other properties this varies with the thermal history of the specimen. After heating to  $700^\circ$  and cooling slowly, fairly reproducible values are obtained of about 6.6 microhms at  $20^\circ$  (Lewis, Physical Rev. 1929, [ii], 33, 284).

**SPECTRA.**—The chief lines in the emission spectrum of neutral and singly ionised beryllium are as follows:

**Be I.** 8254.1, 4572.69, 4407.91, 3865.74, 3865.50, 3865.43, 3865.14, 3321.35, 3321.09, 3321.01, 3019.60, 3019.51, 3019.34, 2986.62, 2986.44, 2986.09, 2650.78, 2650.71, 2650.64,

2650-61, 2650-57, **2650-47**, **2494-59**, 2494-55, **2494-44**, 2350-83, 2350-69, **2348-61**, 2175-07, 2174-94.

**Be II.** 5270-84, 5270-32, 4673-46, 4361-03, 4360-69, 3274-64, 3241-84, 3241-65, 3197-16, **3181-06**, 3046-68, 3046-52 (Paschen and Kruger, *Ann. Physik*, 1931, [v], **8**, 1005). The wavelengths in bold type are important in the analysis of alloys by arc spectra (F. Twyman and D. M. Smith, "Wave Length Tables," A. Hilger, London, 1931).

For lines corresponding to **Be III** and **Be IV** and also for series relationships, see Robinson (*Physical Rev.* 1936, [ii], **50**, 99), Kruger and Cooper (*ibid.* 1933, [ii], **44**, 418), Edlén (*ibid.* 1928, [ii], **33**, 16, 1093), Selwyn (*Proc. Physical Soc.* 1929, **41**, 392).

**CHEMICAL PROPERTIES.**—As the first member of the second group of the Periodic Table beryllium exhibits bivalency, while in its properties it is more nearly related to the zinc sub-group than to that of the alkaline earths. Possessing a strong affinity for oxygen, the freshly polished metal soon tarnishes in air and when finely divided it burns brilliantly on heating in air or oxygen. Combination with the appearance of flame also occurs if the metal is heated in the halogens, in sulphur vapour or if melted with selenium. Hydrogen does not attack it, but nitrogen, ammonia or cyanogen react with the heated metal to form a nitride. Combination with carbon at high temperatures produces a carbide.

Beryllium is resistant to attack by hot or cold water and cold conc. nitric acid although the diluted acid affects it slightly. Warm nitric acid dissolves the metal, but addition of the chloride of a noble metal, e.g. **PtCl<sub>4</sub>**, increases its resistance. Both hydrochloric and sulphuric acid readily attack beryllium, which also dissolves in conc. alkalis in the cold and in dilute alkalis on warming.

**ALLOYS.**—Although it might have been expected that additions of beryllium with its high modulus of elasticity would lead to an improvement in the mechanical properties of other light metals the results have been disappointing. It does not alloy with magnesium and while small additions to aluminium increase the hardness and resistance to wear, the effects are not so good as those produced by silicon or magnesium. With aluminium beryllium forms a eutectic at 644° containing 1.1% of the latter; the solubility at room temperature is very small.

More interesting results have been obtained by the addition of small amounts of beryllium to the heavy metals and much attention has been given to the beryllium bronzes and nickel-beryllium alloys. The bronzes containing about 2.25–2.5% beryllium, when heated at 800° for 1 hour and quenched in water, are softer than copper and easier to work, while heat treatment produces great hardness and elasticity. As such alloys possess considerable resistance to wear and fatigue they make excellent springs and are also recommended for moulding dies, hypodermic syringes, electric switches, clock bearings, etc. The inclusion of small amounts of manganese, cobalt and many other metals has been

suggested to increase the electrical conductivity of the bronzes and to decrease the amount of beryllium necessary to produce such excellent mechanical properties. For a general description of these alloys, see Gadeau, *Rev. Mét.* 1935, **32**, 627; Hessenbruch, *Metallwirts.* 1938, **17**, 541; Sawyer and Kjellgren, *l.c.*; Met. and Alloys, 1940, **11**, 163).

#### BERYLLIUM AND HYDROGEN.

No hydride of beryllium has been isolated, but the arc produced between beryllium electrodes in dry hydrogen gives a spectrum containing two band systems, one between 4800Å and 5120Å due to the **BeH** molecule and the other between 1882Å and 3600Å produced by the ionised molecule **BeH<sup>+</sup>**. Similar bands have been observed for the deuteride (W. W. Watson *et al.*, *Physical Rev.* 1928, [ii], **31**, 1130; **32**, 600; 1929, [ii], **34**, 372; 1931, [ii], **37**, 167; 1937, [ii], **52**, 318; Koontz, *ibid.* 1935, [ii], **48**, 707).

#### BERYLLIUM AND OXYGEN.

**Beryllium Oxide, BeO.**—Formed when the finely divided metal, sulphide or iodide burns in air or oxygen. It is more conveniently prepared by dehydrating the hydroxide at 300–400° or igniting the carbonate at 1,100°. The nitrate or sulphate may also be employed, but long heating is necessary to remove the last traces of oxides of nitrogen or sulphur. Beryllium oxide is a white, amorphous powder which may be obtained crystalline, as hexagonal pyramids isomorphous with zinc oxide, either by dissolving it at red heat in alkali sulphates or by fusion or sublimation (Zachariasen, *Z. physikal. Chem.* 1926, **119**, 204; Mallard, *Compt. rend.* 1895, **105**, 1267). Although the melting-point is about 2,500° the oxide begins to volatilise slowly above 320° while at 2,000° the loss is rapid. The density varies between 2.86 and 3.04, depending on the previous history of the specimen. The heat of formation is 135.9 kg.-cal. and the mean index of refraction 1.723.

Beryllium oxide remains unchanged when heated in chlorine, bromine or iodine; with fluorine a fluoride is formed. It is not easily reduced on heating with metals although reduction seems easier if there is present a metal with which beryllium alloys readily. Ease of attack by acids and alkalis depends on the temperature to which the oxide has been subjected; it dissolves easily in fused alkalis or alkali carbonates or pyrosulphates.

**Beryllium Hydroxide.**—White, voluminous, gelatinous precipitate formed when alkali hydroxides, ammonia, amines or ammonium sulphide act on solutions of beryllium salts; alkali carbonates produce mixtures of carbonate and hydroxide. The moist precipitate readily absorbs **CO<sub>2</sub>** from air and must, therefore, be washed and dried in an atmosphere free from this gas. Dried at ordinary temperature the hydroxide has an indefinite water content, but heating to 150° gives a product corresponding to **Be(OH)<sub>2</sub>**. The amorphous material slowly changes into a denser and more granular crystalline, but metastable, form on standing in air or under water; this is known as the  $\alpha$ -hydroxide.

It is more readily obtained from the gelatinous product by electrodialysis or by heating in solutions of alkalis, alkali carbonates or ammonia. A quantitative precipitation is achieved by heating a neutral solution of a beryllium salt with ammonium nitrate and methyl alcohol, air being simultaneously passed through the mixture (Haber and van Oordt, *Z. anorg. Chem.* 1904, **38**, 380; Havestadt and Fricke, *ibid.* 1930, **188**, 357; Moser and Singer, *Monatsh.* 1927, **48**, 676).

In contact with bases and in the cold the metastable  $\alpha$ -form changes into a stable, crystalline  $\beta$ -form which also results when a hot saturated solution of the amorphous hydroxide in 10N-NaOH is slowly cooled (Fricke, *Z. anorg. Chem.* 1927, **166**, 245; 1929, **178**, 400).

As might be expected, the amorphous product is more reactive than the crystalline forms. Unlike them it absorbs  $\text{CO}_2$  from the air, is soluble in alkali carbonates, dilute mineral and organic acids and in certain beryllium salts. The crystalline modifications require higher concentrations of alkalis to dissolve them and the solutions contain beryllates of the type  $\text{M}'_2\text{BeO}_2$  ( $\text{M}' = \text{Na}$  or  $\text{K}$ ); the amorphous form under like conditions partly yields beryllates and partly gives a colloidal solution (Hantzsch, *Z. anorg. Chem.* 1920, **30**, 303, 319; Mohanlal and Dhar, *ibid.* 1928, **174**, 1; Fricke *et al.*, *ibid.* 1932, **205**, 127, 287).

#### BERYLLIUM AND HALOGENS.

**Beryllium Fluoride,  $\text{BeF}_2$ .**—Formed by heating the carbide or oxide in fluorine or hydrogen fluoride, it is usually made by slowly heating dry ammonium beryll fluoride,  $(\text{NH}_4)_2\text{BeF}_4$ , to a red heat in a current of  $\text{CO}_2$  (Lebeau, *Ann. Chim. Phys.* 1899, [vii], **16**, 484). The product is a transparent, vitreous mass,  $d_4^{25} = 1.986$ , which shows no regular structure but has a "random network" (Warren and Hill, *Z. Krist.* 1934, **89**, 481). It has no definite melting-point but is fluid at  $800^\circ$  and begins to volatilise at that temperature giving a white crystalline sublimate; the molten product is a poor conductor of electricity. The fluoride dissolves in water with hydrolysis so that, like the other halides, it cannot be produced from aqueous solution. It is slightly soluble in absolute alcohol and more so in a mixture of alcohol and ether. No combination occurs with anhydrous hydrofluoric acid so that the acid,  $\text{H}_2\text{BeF}_4$ , corresponding to the beryll fluorides is apparently not produced. With liquid or gaseous ammonia a monamine,  $\text{BeF}_2 \cdot \text{NH}_3$ , is formed (Biltz and Rahlfs, *Z. anorg. Chem.* 1927, **166**, 351, 355, 361, 367). The fluoride differs from the other beryllium halides in that addition of sodium hydroxide does not precipitate the hydroxide but yields a sparingly soluble double salt.

Evaporation of an aqueous solution of beryllium fluoride and heating the product to  $300\text{--}800^\circ$  gives a white mass of the oxyfluoride,  $2\text{BeO} \cdot 5\text{BeF}_2$ , which is an important intermediate in the production of the metal from its ores; it is completely soluble in water.

**Beryll fluorides.**—Numerous double compounds of the type  $\text{M}'_2\text{BeF}_4$  and  $\text{M}'\text{BeF}_4$

have been obtained and are interesting in that many of them are isomorphous with the corresponding sulphates. They are usually made by one of the following methods: (a) concentrating a solution containing the two fluorides in the correct proportions; (b) dissolving stoichiometric amounts of beryllium oxide and the metal carbonate or hydroxide in a slight excess of hydrofluoric acid; (c) from ammonium or silver beryll fluoride by double decomposition. Like the corresponding sulphates the alkaline earth and lead salts are sparingly soluble but the silver salt is very soluble in water. Acid salts of the type  $\text{M}'\text{HBeF}_4$  and more complex double compounds, including aminoberyll fluorides, have been prepared while by fusion methods the compounds  $\text{M}'\text{BeF}_3$  ( $\text{M}' = \text{Na}$  or  $\text{K}$ ) have been obtained (Marignac, *Ann. Chim. Phys.* 1873, [iv], **30**, 55; N. Rây, *Z. anorg. Chem.* 1931, **201**, 289; 1932, **205**, 257; 206, 209; 1936, **227**, 32, 103; 1939, **241**, 165; Hultgren, *Z. Krist.* 1934, **88**, 233).

**Beryllium Chloride.**—Beryllium ignites on gently heating in chlorine and the resulting chloride is deposited as a sublimate of white needles. It is also produced by heating the carbide or intimate mixtures of the oxide and sugar charcoal in chlorine or hydrogen chloride at  $1,000^\circ$ . Phosgene readily reacts with beryllium oxide at  $900^\circ$ , but below  $500^\circ$  the reaction is so slow that it is possible to remove alumina and ferric oxide by heating the crude beryllia in this gas at  $450^\circ$  since aluminium and ferric chlorides are volatile at this temperature.

Beryllium chloride melts at  $405^\circ$  and begins to volatilise near this temperature; the boiling-point is given as  $488^\circ$ . The vapour pressure at the boiling point indicates about 50% association to  $\text{Be}_2\text{Cl}_4$ . The molten chloride is practically a non-conductor of electricity but additions of alkali chlorides rapidly increase the conductivity (Fischer and Rahlfs, *Z. Elektrochem.* 1932, **38**, 592; *Z. anorg. Chem.* 1933, **211**, 321). Beryllium chloride is very hygroscopic and is easily hydrolysed in aqueous solution. It is insoluble in benzene, carbon disulphide, chloroform or carbon tetrachloride although it is soluble in many other organic media (e.g.  $\text{MeOH}$ ,  $\text{EtOH}$ ), often with combination (e.g. *o*-toluidine) to produce molecular compounds of the type  $\text{BeCl}_2 \cdot n\text{Y}$  where Y is the solvent molecule and  $n$  is usually 2 or 4 (R. Fricke *et al.*, *Z. anorg. Chem.* 1925, **146**, 103, 121; 1926, **152**, 347; 1927, **163**, 31; 1928, **170**, 257).

Thermal analysis indicates that double compounds of the type  $\text{M}'_2\text{BeCl}_4$  or  $\text{M}'\text{BeCl}_4$  are formed with alkali and barium chlorides respectively; thallous chloride forms  $\text{TlBe}_2\text{Cl}_6$ . Complex formation also occurs with certain other chlorides (J. M. Schmidt, *Bull. Soc. chim.* 1926, [iv], **39**, 1686; *Ann. Chim.* 1929, [x], **11**, 351). Prytz (*Z. anorg. Chem.* 1937, **231**, 238) was unable to secure evidence of any complex formation in aqueous solutions of beryllium chloride containing potassium chloride.

When an aqueous solution of beryllium chloride is evaporated over sulphuric acid and in an atmosphere of hydrogen chloride there are deposited colourless crystals of the hydrated



chloride  $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ . The tetrahydrate is extremely hygroscopic and readily loses  $\text{HCl}$  in damp air; it is more stable in dry air and can be kept over phosphorus pentoxide without losing water of crystallisation (Debray, *Ann. Chim. Phys.* 1855, [iii], 44, 22; Mieleitner and Steinmetz, *Z. anorg. Chem.* 1913, 80, 73; Fricke and Schützdeller, *ibid.* 1923, 131, 136; Čupr and Šalanský, *ibid.* 1928, 176, 241). Mieleitner and Steinmetz state that the hydrated chloride is formed when hydrogen chloride is led into the aqueous solution mixed with ether, but Čupr and Šalanský on repeating this work obtained, instead, white needles of the compound  $[\text{Be}(\text{H}_2\text{O})_3(\text{C}_2\text{H}_5)_2\text{O}]\text{Cl}_2$ .

Numerous oxychlorides of beryllium have been described, but there is some doubt whether they are definite chemical compounds. The view of Parsons and his collaborators (J. Amer. Chem. Soc. 1904–06) is that all basic salts of beryllium are merely solid solutions of the normal salt in the hydrated hydroxide; *see, however*, beryllium sulphate.

Dry beryllium chloride, cooled in a freezing mixture, reacts with ammonia in the absence of air to form the hexammine  $\text{BeCl}_2 \cdot 6\text{NH}_3$  as a white voluminous powder which deliquesces slowly in air. At  $0^\circ$  the tetrammine is produced, and this is also obtained when ammonia is passed into an ethereal solution of the chloride. Thermal decomposition of the tetrammine above  $210^\circ$  and *in vacuo* yields a diammine which also results from the action of ammonia on beryllium chloride at room temperature (Ephraïm, *Ber.* 1912, 45, 1323; *Z. physikal. Chem.* 1913, 81, 532; Mieleitner and Steinmetz, *l.c.*; Fricke and Havestadt, *Z. anorg. Chem.* 1925, 146, 126; W. Biltz *et al.*, *ibid.* 1925, 148, 158; 1927, 166, 341; Bergstrom, *J. Amer. Chem. Soc.* 1928, 50, 657).

**Beryllium Perchlorate,  $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ .**—Obtained as fine, colourless, deliquescent crystals by double decomposition of barium perchlorate and beryllium sulphate and concentrating the filtered solution with excess of perchloric acid (Čupr, *Coll. Czech. Chem. Comm.* 1929, 1, 377). The solubility of the anhydrous salt at  $25^\circ$  is 59.5% (Sidgwick and Lewis, *J.C.S.* 1926, 1290).

**Beryllium Bromide,  $\text{BeBr}_2$ .**—Obtained as long white needles by methods analogous to those used for the chloride which it resembles closely in properties. The melting-point is  $487^\circ$  although sublimation begins at  $473^\circ$ ; the density at  $25^\circ$  is 3.465. The fused bromide is a non-conductor of electricity.

With liquid hydrogen sulphide at  $-78.5^\circ$  the bromide forms a compound  $\text{BeBr}_2 \cdot 2\text{H}_2\text{S}$  while with ammonia it forms amines containing 10, 6 and 4 mol.  $\text{NH}_3$ ; the tetrammine alone is stable at room temperature.

Beryllium bromide tetrahydrate is produced similarly to the chloride and forms hygroscopic cubic crystals. A trihydrate-etherate,  $\text{BeBr}_2 \cdot 3\text{H}_2\text{O} \cdot (\text{C}_2\text{H}_5)_2\text{O}$ , is also known.

**Beryllium Iodide,  $\text{BeI}_2$ .**—M.p.  $480^\circ$ ; b.p.  $\sim 590^\circ$ ; sublimation temp.  $488^\circ$ ;  $d_4^{25} = 4.325$ .

Prepared by similar methods to the chloride and bromide, but higher reaction temperatures

are needed. It sublimes to form white needles which are very sensitive to moisture, deliquescing and losing hydrogen iodide in moist air. The iodide is more susceptible to oxidation than the other halides and takes fire if heated to red heat in air or oxygen; it is safer, therefore, to sublime it in a high vacuum (Messerknecht and Biltz, *Z. anorg. Chem.* 1925, 148, 152). The other halogens convert the iodide into the respective halides although with fluorine an iodo-fluoride is also produced. Heated in hydrogen sulphide or sulphur vapour beryllium sulphide is formed while with liquid hydrogen sulphide at  $-83^\circ$  the double compound  $\text{BeI}_2 \cdot 2\text{H}_2\text{S}$  is obtained (W. Biltz and Keuncke, *ibid.* 1925, 147, 185, 174).

Beryllium iodide is soluble in water but no hydrate has been isolated apart from a dihydrate-dietherate,  $\text{BeI}_2 \cdot 2\text{H}_2\text{O} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  (Čupr and Šalanský, *l.c.*). Solution in organic media is often accompanied by combination.

Amines containing respectively 13, 6, 4 and  $1\frac{1}{2}$  mol. of ammonia per mol. of iodide have been reported (W. Biltz *et al.*, *ibid.* 1925, 148, 152; 1927, 166, 341; Bergstrom, *l.c.*).

**Beryllium Periodate.**—Evaporation of an aqueous solution of basic beryllium carbonate with periodic acid leads to the separation of thick plates of  $\text{Be}_2(\text{IO}_6)_2 \cdot 11\text{H}_2\text{O}$ ; the salt is decomposed on boiling with water (Atterberg, *Bull. Soc. chim.* 1875, [ii], 24, 358).

#### BERYLLIUM AND SULPHUR.

**Beryllium Sulphide,  $\text{BeS}$ .**—Formed as a grey, amorphous mass when the halides are heated in hydrogen sulphide or sulphur vapour or when finely divided beryllium is burned in sulphur vapour. It is best prepared by heating the powdered metal, covered with sulphur, in a current of hydrogen in a porcelain tube for 10–20 minutes at  $1,000$ – $1,300^\circ$ . The grey, partly sintered mass is apparently more stable in air than products obtained by other methods (Tiede and Goldschmidt, *Ber.* 1929, 62 [B], 758). This material also develops a blue phosphorescence if heated in a high vacuum at  $1,300^\circ$  and then exposed to an arc lamp; this is attributed to the presence of traces of iron.

Beryllium sulphide,  $d$  2.36 (Zachariasen, *Z. physikal. Chem.* 1926, 119, 201) possesses a faint odour of hydrogen sulphide, this gas being easily liberated on treatment with dilute acids. Lebeau states that it is attacked by water, but according to Mieleitner and Steinmetz it is only slowly decomposed even by boiling water. Heated in air or oxygen the sulphide burns, yielding sulphur dioxide and beryllia in the former gas and beryllium sulphate in the latter. Hydrogen does not attack it but chlorine and bromine convert it at a red heat into the respective halides.

**Beryllium Sulphite,  $\text{BeSO}_3$ .**—When freshly precipitated beryllium hydroxide, freed from water by washing with alcohol, is dissolved in alcohol saturated with sulphur dioxide, the solution on evaporation *in vacuo* over sulphuric acid and sodium hydroxide deposits small, colourless, hexagonal crystals of beryllium sulphite. The product is only slightly soluble in alcohol or water but the latter medium soon hydrolyses it,

forming more soluble basic salts (Kruss and Moraht, Ber. 1890, **23**, 734).

**Beryllium Sulphate,  $\text{BeSO}_4$ .**—Prepared by dissolving the oxide or hydroxide in excess of hot conc. sulphuric acid and cooling; the excess acid is decanted from the fine microcrystalline powder which separates; this is washed with alcohol and dried. Removal of excess acid by evaporation leads to slight decomposition and the formation of a little beryllium oxide. This is evident, too, when the sulphate is made by dehydrating the di- or tetrahydrate by heating to  $400^\circ$ .

Beryllium sulphate is very hygroscopic and although not appreciably soluble in cold water it is slowly converted into the soluble tetrahydrate; this process proceeds more rapidly on heating. The density of the salt is 2.443. With dry ammonia there is formed a diammine which passes into a monoammine on heating to  $234^\circ$ .

**Hydrates of Beryllium Sulphate.**—Considerable attention has been given to the system  $\text{BeSO}_4\text{--H}_2\text{O}$  and numerous hydrates have been reported, but the only ones about which there appears to be no doubt are the tetra- and di-hydrates (Parsons and Fuller, Science, 1906, **24**, 202; Taboury, Compt. rend. 1914, **159**, 180; Britton, J.C.S. 1921, **119**, 1967; F. Krauss and Gerlach, Z. anorg. Chem. 1924, **140**, 61; Schreiner and Sieverts, *ibid.* 1935, **224**, 167; Schröder, *ibid.* 1936, **228**, 129; Novoselova and Levina, J. Gen. Chem. Russ. 1938, **8**, 1143).

The tetrahydrate is prepared by dissolving beryllium oxide, hydroxide or carbonate in warm dilute sulphuric acid (*d* 1.07), filtering and concentrating the solution; the crystals which separate on cooling are washed with alcohol. Britton and Allmand also obtained it by treating a strong solution of the nitrate with excess of conc. sulphuric acid and pouring the mixture into alcohol when the tetrahydrate separates (J.C.S. 1921, **119**, 1464). It may be recrystallised from hot dilute sulphuric acid or even hot water. The crystals belong to the tetragonal holohedral class and their density is 1.712. The tetrahydrate is readily soluble in water, 100 g. of the solution containing 29.94 g.  $\text{BeSO}_4$  at  $25^\circ$  (Sidgwick and Lewis, *l.c.*); the solution reacts acid, the salt being appreciably hydrolysed.

Heating the tetrahydrate to  $120^\circ$  or maintaining it at  $93^\circ$  until a constant weight is attained causes the loss of 2 mol. of water; the resulting dihydrate has a similar crystalline form to that of the tetrahydrate. It partly melts on heating to  $158^\circ$  and gradually loses water above  $100^\circ$ . Like the tetrahydrate it is stable at room temperature.

**Double Salts.**—Beryllium sulphate yields double salts with potassium and ammonium sulphate of the type  $\text{BeSO}_4\cdot\text{M}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ . Fused potassium and beryllium sulphates are readily miscible, and from the melt containing 33–60 mol. per cent. of the latter there can be crystallised the double salt  $\text{K}_2\text{SO}_4\cdot 2\text{BeSO}_4$ .

A study of the isotherms of the system  $\text{BeSO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$  between  $0^\circ$  and  $100^\circ$  reveals the existence of the compound  $\text{BeSO}_4\cdot 3\text{Na}_2\text{SO}_4$  which is stable above  $42^\circ$  (Grahmann, Z. anorg. Chem. 1913, **81**, 265; Marchal, J. Chim. phys. 1925, **22**, 516; Schröder,

Z. anorg. Chem. 1938, **239**, 39, 225; 1939, **241**, 179).

**Basic Beryllium Sulphates.**—Parsons and his collaborators hold the view that all basic salts of beryllium consist of solid solutions of the salt in hydrated beryllium hydroxide, but Sidgwick and Lewis (J.C.S. 1926, 1298), finding that approximately 4 mol. of the oxide will dissolve in 1 mol. of beryllium sulphate, suggest that beryllia may replace water in  $[\text{Be}_4\text{H}_2\text{O}]_2\text{SO}_4$ . There will thus be formed the complex  $[\text{Be}_4\text{BeO}]_2\text{SO}_4$  although, actually, the replacement may take place in stages. Such basic salts have not, however, been obtained crystalline, but only as syrupy masses when solutions of beryllium hydroxide or carbonate in aqueous solutions of the normal salts are concentrated.

#### BERYLLIUM AND SELENIUM.

**Beryllium Selenide,  $\text{BeSe}$ .**—Grey crystalline mass obtained by leading hydrogen carrying selenium vapour over the heated metal. The product is soluble in water but the solution soon decomposes with deposition of selenium (Zachariasen, Z. physikal. Chem. 1926, **124**, 278, 437; Pauling, J. Amer. Chem. Soc. 1927, **49**, 787).

**Beryllium Selenite,  $\text{BeSeO}_3\cdot 2\text{H}_2\text{O}$ .**—Obtained as a precipitate on adding a solution of neutral sodium selenite to one of beryllium sulphate. The salt, after filtering and washing, is treated with selenious acid until neutral and dried at  $60^\circ$ . The acid salts  $\text{BeSeO}_3\cdot \text{H}_2\text{SeO}_3$  and  $\text{BeSO}_3\cdot 2\text{H}_2\text{SeO}_3$  are also known (Nilson, Ber. 1875, **8**, 655).

**Beryllium Selenate.**—Treatment of an aqueous solution of basic beryllium carbonate with the requisite amount of selenic acid and evaporation of the solution gives rise to colourless rhombic crystals of  $\text{BeSeO}_4\cdot 4\text{H}_2\text{O}$  from which the anhydrous salt may be obtained by heating to  $300^\circ$ . At  $100^\circ$  2 mol. of water are removed and the dihydrate produced. These compounds closely resemble the corresponding sulphates, the tetrahydrates being isomorphous (Topsoë, Ber. Wien Akad. 1872, [ii], **66**, 5; Atterberg, Bull. Soc. chim. 1873, [ii], **19**, 498; Sidgwick and Lewis, *l.c.*).

#### BERYLLIUM AND TELLURIUM.

The telluride is obtained in a like manner to the selenide and is a grey powder, *d* 5.09. It is slowly decomposed by moist air and readily by water with evolution of hydrogen telluride.

Beryllium tellurite and tellurate are stated to form white precipitates on treating solutions of beryllium salts with alkali tellurite or tellurate respectively (Berzelius, Ann. Chim. Phys. 1835, [ii], **58**, 244, 259). These are probably basic salts, for Montignie (Bull. Soc. chim. 1935, [v], **2**, 864) assigns to the tellurate the formula  $\text{BeTeO}_4\cdot 7\text{Be}(\text{OH})_2$ .

#### BERYLLIUM AND NITROGEN.

**Beryllium Nitride,  $\text{Be}_3\text{N}_2$ .**—Beryllium combines with nitrogen at temperatures above  $900^\circ$ , but even at  $1,100^\circ$  the reaction is slow and the product contains appreciable amounts of metal; a better result is obtained when ammonia is substituted for nitrogen. The nitride formed in

these methods is a grey powder, but a white product is made by passing cyanogen over the metal at 800°. Heating beryllium carbide in nitrous oxide or with ammonium nitrate yields an equally pure material.

Beryllium nitride melts at about 2,200° and begins to dissociate above this temperature. The melt, on cooling, solidifies to colourless cubic crystals which scratch glass, are stable in air and only slowly decomposed by boiling water; dilute acids and concentrated alkalis readily decompose it. When mixed with alumina the nitride develops a strong phosphorescence after exposure to a mercury vapour lamp (Fichter and Brunner, *Z. anorg. Chem.* 1915, **93**, 89; Neumann *et al.*, *ibid.* 1932, **204**, 81; Vournasos, *Bull. Soc. chim.* 1917, [iv], **21**, 282; Satoh, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **29**, 41; 1938, **34**, 888; Stackelberg and Paulus, *Z. physikal. Chem.* 1933, **B**, **22**, 305).

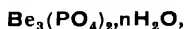
**Beryllium Nitrate.**—The anhydrous salt has not yet been isolated, but hydrates containing 4 and 3 mol. of water have been prepared while the existence of a mono- and dihydrate has been inferred from tensimetric data. The tetrahydrate is obtained either by dissolving beryllium hydroxide in nitric acid ( $d$  1.52) at 0° and allowing the solution to evaporate in air or by repeated evaporation of the basic acetate with conc. nitric acid, adding fuming acid and seeding the solution. It forms deliquescent crystals which melt at 61°. If crystallisation takes place from a solution more dilute in nitric acid, colourless prisms of the trihydrate are obtained. Attempts to dehydrate these products result in loss of oxides of nitrogen (Parsons, *Science*, 1907, **25**, 402; Haase, *Z. Krist.* 1927, **65**, 537; Sieverts and Petzold, *Z. anorg. Chem.* 1933, **212**, 49; Novoselova and Nagorskaja, *Bull. Soc. chim.* 1935, [v], **2**, 967).

No double compounds with alkali nitrates have been reported, but the existence of such compounds in solution has been inferred by Chauvenet (*Compt. rend.* 1939, **208**, 194; 1940, **210**, 250).

#### BERYLLIUM AND PHOSPHORUS.

**Beryllium Phosphide.**—Formed when beryllium is heated in phosphorus vapour. Both Wohler and Lebeau state that it is obtained when phosphine acts on heated beryllium chloride, but Høltje and Meyer (*Z. anorg. Chem.* 1931, **197**, 93) could not induce combination even at high temperature and pressure.

**Beryllium Phosphates.**—According to F. Travers and Perron (*Ann. Chim.* 1924, [x], **1**, 318) the hydrated orthophosphate,



is formed as a dense, white, microcrystalline precipitate by adding a dilute aqueous solution of disodium phosphate to one of beryllium sulphate until a faint turbidity appears and then heating the solution. Excess of the sodium phosphate solution produces an amorphous, white precipitate also stated to be the orthophosphate; the tetrahydrate is said to separate on crystallising from dilute acetic acid. Heating the tetrahydrate at 100° produces a trihydrate while

much higher temperatures are needed for complete dehydration.

**Primary Beryllium Hydrogen Phosphate,  $\text{BeH}_4(\text{PO}_4)_2$ ,** separates as hygroscopic, colourless plates on evaporating a solution of the oxide in a slight excess of the calculated amount of phosphoric acid. The *secondary phosphate,  $\text{BeHPO}_4$ ,* is apparently incapable of existence and disproportionates readily into the primary and tertiary salts. The ammonium salt,  $\text{NH}_4 \cdot \text{BePO}_4 \cdot \text{H}_2\text{O}$ , is, however, known and is the precipitate obtained on treating neutral or slightly acid solutions of beryllium salts with ammonium phosphate. It is sufficiently insoluble to provide a method of estimating the metal, the precipitate being converted into the pyrophosphate,  $\text{Be}_2\text{P}_2\text{O}_7$ , by ignition (Travers and Perron, *loc. cit.*). A beryllium metaphosphate has also been reported (Bleyer and Muller, *Z. anorg. Chem.* 1913, **79**, 273).

#### BERYLLIUM AND ARSENIC.

When beryllium is heated in arsenic vapour a grey product is formed which is probably the arsenide, for it liberates arsine with water.

**Beryllium Arsenate,  $\text{Be}_3(\text{AsO}_4)_2 \cdot 16\text{H}_2\text{O}$ ,** is prepared by adding an aqueous solution of the sulphate to one of disodium hydrogen arsenate acidified with acetic acid and air-drying the precipitate.

The acid salts  $\text{BeH}_4(\text{AsO}_4)_2$  and  $\text{BeHAsO}_4$  have also been made as well as numerous basic salts (Bleyer and Muller, *ibid.* 1912, **75**, 288; Ephraim and Rossetti, *Helv. Chim. Acta*, 1920, **12**, 1033).

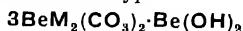
#### BERYLLIUM AND CARBON.

**Beryllium Carbide,  $\text{Be}_2\text{C}$ .**—Beryllium possesses considerably affinity for carbon, particularly at high temperatures, and a carbide is readily formed on heating the metal at 1,300–1,400° with carbon or in CO or CO<sub>2</sub>. The usual method of preparation is to heat, in an electric furnace, intimate mixtures of beryllia and sugar charcoal bonded together with an agent such as dextrin. The product is cleaned by treating with hot dilute hydrochloric acid to remove adhering oxide and carbon. It forms regular, brick-red, octahedral or hexagonal crystals hard enough to scratch glass and of density 1.9. Moist air and water slowly decompose it with liberation of methane. The carbide suffers only a superficial attack when heated in oxygen, nitrogen, phosphorus or iodine vapour, but the other halogens as well as their hydrides decompose it fairly readily at 800° as also does sulphur vapour at 1,000°. Hot aqueous mineral acid solutions attack it more easily when dilute, while with hot caustic alkali there is a rapid evolution of methane (Lebeau, *Compt. rend.* 1895, **121**, 496; Fichter and Brunner, *Z. anorg. Chem.* 1915, **93**, 91; Messerknecht and Biltz, *ibid.* 1925, **148**, 153; Schmidt, *Bull. Soc. chim.* 1928, [iv], **43**, 49; Stackelberg and Quatram, *Z. physikal. Chem.* 1934, **B**, **27**, 50).

**Beryllium Acetylide,  $\text{BeC}_2$ .**—Produced when acetylene is led over powdered beryllium at 450°; it differs from the carbide in regenerating acetylene when treated with water or dilute

hydrochloric acid (Durand, Bull. Soc. chim. 1924, [iv], 35, 1141).

**Beryllium Carbonate.**—Freshly precipitated beryllium hydroxide readily absorbs atmospheric carbon dioxide, while if an aqueous suspension of the hydroxide is saturated with the gas there is formed the basic carbonate  $3\text{Be}(\text{OH})_2 \cdot \text{BeCO}_3$ . Basic salts of somewhat indefinite composition are also produced as white precipitates on adding aqueous sodium or ammonium carbonate to solutions of beryllium salts. If carbon dioxide is passed for a long time into a suspension of one of these basic carbonates and the solution filtered and evaporated over  $\text{H}_2\text{SO}_4$  in an atmosphere of  $\text{CO}_2$ , white hexagonal crystals are obtained which are said to be the tetrahydrate of the normal salt  $\text{BeCO}_3 \cdot 4\text{H}_2\text{O}$  (Jahresber. 1868, 203). The crystals effloresce in air, are not very soluble in water and lose carbon dioxide as well as water on drying at  $100^\circ$ ; the residual basic carbonates do not begin to decompose until about  $200^\circ$ . Beryllium carbonates are soluble in excess of alkali or ammonium carbonate and from the solutions alcohol precipitates crystalline compounds of the type



(M=alkali metal or  $\text{NH}_4$ ). The amount of hydroxide seems to vary in different preparations so that possibly it is merely an impurity in the true double salts  $\text{M}_2\text{CO}_3 \cdot \text{BeCO}_3$ . Heating the solutions redeposits the basic beryllium carbonate (Klatzo, J. pr. Chem. 1869, [i], 106, 227; Debray, Ann. Chim. Phys. 1855, [iii], 44, 32; Atterberg, Svenska Akad. Handl. 1873, 12, 31; Parsons, J. Amer. Chem. Soc. 1904, 26, 721; Venturello, Gazzetta, 1939, 69, 73).

#### BERYLLIUM SALTS OF ORGANIC ACIDS.

Numerous beryllium salts of organic acids have been made; in some cases, for example with oxalic acid, the normal salt is known while with other acids only basic salts have been obtained. The most important of these is the basic acetate, for its ready solubility in chloroform provides a means of separating beryllium from many other metals, including iron and aluminium.

##### Basic Beryllium Acetate,



Separates as octahedral crystals on cooling a solution of the hydroxide in excess of hot, strong acetic acid. The crude product is recrystallised from chloroform until the melting-point is  $286\text{--}287^\circ$  or it may be purified by sublimation *in vacuo* (Urban and Lacombe, Compt. rend. 1901, 133, 874; 1902, 184, 772; Tanatar, J. Russ. Phys.-Chem. Soc. 1904, 36, 82; Haber and van Oordt, Z. anorg. Chem. 1904, 40, 465; Kling and Gelin, Bull. Soc. chim. 1914, [iv], 15, 205).

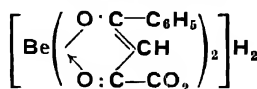
The physical and chemical properties of the salt indicate that it is a non-ionised covalent complex, while X-ray examination demonstrates that the four beryllium atoms occupy the apices of a regular tetrahedron in the centre of which is the single oxygen atom; the acetate radicals span the six edges (W. Bragg and Morgan, Proc.

Roy. Soc. 1923, A, 104, 437; Morgan and Astbury, *ibid.* 1926, A, 112, 444; Pauling and Sherman, Proc. Nat. Acad. Sci. 1934, 20, 340).

The basic acetate is stable to air and is insoluble in, and unaffected by, cold water; warm water dissolves it with decomposition. It is soluble in many organic solvents.

Normal beryllium acetate is said to be formed when the basic salt is heated at  $140^\circ$  in a sealed tube with acetic acid and acetic anhydride; it is insoluble both in cold water and organic solvents (Tanatar, *l.c.*; Steinmetz, Z. anorg. Chem. 1907, 54, 219).

Most of the monobasic organic acids give definite basic salts analogous to the acetate, but with di- and tribasic acids the more indefinite types experienced with inorganic acids are obtained. With the monobasic organic acids, however, normal salts are also known. The beryllium derivative of benzoylpyruvic acid,



has been resolved into two forms with opposite and fugitive mutarotations (Mills and Gotts, J.C.S. 1926, 3121).

##### Beryllium Acetylacetone, $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ .

—Prepared either by the action of acetylacetone on aqueous or boiling alcoholic suspensions of beryllium carbonate or by treating aqueous beryllium chloride solution with an ammoniacal solution of the diketone followed by further careful addition of ammonia (Jaeger, Rec. trav. chim. 1914, 33, 394; Parsons, Z. anorg. Chem. 1904, 40, 412; W. Biltz, Annalen, 1904, 331, 336). It may be purified by sublimation or by crystallisation from alcohol. Slightly soluble in cold water it dissolves readily in the hot medium, but with gradual decomposition and deposition of the hydroxide; it is soluble in many organic solvents. The acetylacetone does not form an additive compound with ammonia although with  $\text{SO}_2$  a 1:1 compound is formed. The ethylacetoacetate behaves similarly (Booth and Smuley, J. Physical Chem. 1933, 37, 171).

#### ORGANOMETALLIC DERIVATIVES OF BERYLLIUM.

Few such derivatives are known, none of them being analogous to the Grignard reagents produced with magnesium.

*Beryllium dimethyl, diethyl and dibutyl* have been prepared from beryllium chloride and the appropriate Grignard reagent; the first-named is also formed when mercury dimethyl acts on beryllium. The diethyl and dibutyl compounds are liquids while the dimethyl is a high-melting solid subliming at  $200^\circ$ .

*Beryllium diphenyl and di-p-tolyl* have been obtained (Schulze, Iowa State Coll. J. Sci. 1933, 8, 225).

For the detection and estimation of beryllium, v. CHEMICAL ANALYSIS, Vol. II, 580a and 587 b, c, d.

G. R. D.

GLUCOCHLORAL (v. Vol. III, 35c).  
GLUCONIC ACID (v. Vol. II, 297a).

**GLUCOSANS** (v. Vol. II, 295b).

**GLUCOSE** (v. Vol. II, 284a).

**GLUCOSEEN-5:6** (v. Vol. II, 294d).

**GLUCOSIDASE** (v. Vol. IV, 313b, 314b).

**GLUCOSIDES** (v. GLYCOSIDES).

**GLUCOXYLOSE** (v. Vol. II, 300c).

**GLUCURONIC ACID** (v. Vol. II, 297c).

**GLUE AND GLUE TESTING.** Glue or gelatin adhesives are materials which have the property of gelatinising in aqueous solution and drying to form a hard strongly adhesive layer. They are obtained from the collagenous parts of animals and fish, chiefly hide and skin trimmings, bones, cartilage and tendons, by extraction with water. Keratinous materials such as muscles, horns and hoofs contain little, if any, glue-yielding material, but horn-piths give ossein.

Other preparations which possess this adhesive property are also loosely termed glues, e.g. *marine glue*, a mixture of rubber and asphaltum, gluten and casein glues, mineral and vegetable glues, blood and albumin glues, phenol-formaldehyde condensation products, etc., but, strictly speaking, these have no claim to that name, as they contain no gelatin.

Gelatin is the principal constituent of a glue, and therefore many of the properties of the latter depend on those of the former. This, however, is not always the case; highly purified gelatin is distinctly weaker, as an adhesive, than a commercial gelatin or a high grade glue. The superior adhesive power of the latter may be due to the presence of other soluble products which in themselves possess no adhesive properties, but which modify those of the gelatin by altering its state of aggregation.

Glue and gelatin do not exist, as such, in the animal organism but are the products of the hydrolysis of various nitrogenous components brought about by boiling water.

These components may be classed as follows:

(1) *Collagens*.—The organic materials of hides, skins, bones, tendons and cartilage. Hofmeister regarded collagens as anhydrides of gelatin. According to Grassmann (J. Soc. Leather Trades' Chem. 1938, 22, 473) the fibres exist in different forms, dependent on the stretching or folding of the polypeptide chains. Küntzel (Magyar Timar. 1938, 1; J. Soc. Leather Trades' Chem. 1938, 22, 410) regards the formation of gelatin as a type of melting process. In the molten or gummy condition the individual molecules are unstable and pass from the stretched into the coiled-up condition.

(2) *Keratins*.—Found in the hard structure of the nails, hair, horns, hoofs, whale-bone, etc. They are unaffected by boiling water except under pressure, yield products which have little gelatinising power and are not used in glue manufacture.

(3) *Elastins*.—Mainly derived from tendons and ligaments. They are similar to the keratins in behaviour in water but are acted on by trypsin and other enzymes. Liming with arsenic limes swells and breaks these tissues (W. T. Roddy and F. O'Flaherty, J. Amer. Leather Chem. Assoc. 1938, 33, 257).

(4) *Reticulin*.—The collagen fibres of hides are held together by a meshwork of reticulin

and elastin fibres. Collagen fibres are covered with a fine sheath of reticular tissue, which is stronger in young skins than in old ones. It is very susceptible to bacteria, broken by hydrochloric acid solutions of  $p_H < 2$ , weakened by sodium hydroxide or sodium sulphide and more slowly by calcium hydroxide.

(5) *Mucins and Mucoids*.—A class of glycoproteins, insoluble in water but easily soluble in dilute alkalis, which is present to a small extent in tendons, connective tissue of hides and skins, cartilage and bones.

(6) *Chitin*.—Found in the hard sheaths of beetles, locusts, shrimps, crabs, etc. It can be converted into a gelatinous form by treatment with acids but is of no utility.

For convenience the products obtained from collagens by the action of water may be classed into gelatin, chondrin and mucin, the properties of which will be described later. During the extraction of glue, or gelatin, two reactions take place: (a) hydrolysis of ossein or collagen to form gelatin; (b) hydrolysis of gelatin giving harmful degradation products.

The extraction process appears to be, therefore, a very simple one. In practice it is not so because, unless properly controlled, the second reaction, although slower than the first, will tend to produce larger quantities of those materials which impair the properties of the finished product and especially the adhesiveness. It follows therefore that, whatever the glue-yielding material used, the following precautions should be observed:

(a) The extraction should be carried out as rapidly and at as low a temperature as is consistent with economic working.

(b) The acids or alkalis used in the preliminary treatment of the bones or hide trimmings should be removed as completely as possible.

(c) The extracting water should be as nearly neutral as possible. Distilled water is always to be preferred, and for the gelatin maker it is almost a necessity.

Many other factors influence the properties of glue, but will be considered later, as they relate to processes which follow the extraction.

Of the materials mentioned, tannery by-products and bones are those most commonly used; horn-piths are used for the production of special glues in which great adhesiveness is not necessary.

**MANUFACTURE:** (a) *Hide and Skin Glues*.

—While the epidermis of the hide yields little or no glue, the *corium* or inner skin, consisting mainly of collagen fibres, gives a high grade glue. Hides and skins are, however, only used for this purpose when unfit for leather manufacture. The following are the raw materials in decreasing order of quality: hide pieces of calf, goat, deer, etc., including ear and face clippings; low grade de-woolled sheepskins; sheep "spetches"; hand and machine trimmings and fleshings from hides and skins; foreign sheep "spetches"; and foreign hide and skin fleshings. Good tannery pieces ("spetches") yield about 45% of glue while fleshings only give 20–30%. Rabbit skins yield a pale coloured glue which has a good adhesive power, but a weaker jelly strength than best hide glue. Glues

from the skins of young and small animals contain more *chondrin* (*q.v.*) and are weaker in jelly strength than glues from older and larger animals. The pieces and trimmings may be unlimed or limed. Many patents exist for making glue from tanned leathers, but the cost of the previous de-tanning is considerable. In the manufacture of high class glues, much discretion is required in blending the raw materials.

The unlimed raw materials are obtained from the tannery or from the animals at the slaughterhouse. If not used immediately they must be washed and salted, salted and dried, or limed to prevent putrefaction. Before liming, they are washed in a machine to remove blood and dirt, which would either produce a highly coloured glue or reduce its adhesive properties, and they are often run through shredding or cutting machines to ensure a more uniform action of the lime.

The limed raw materials are cut from hides which have been laid flat in pits in liquors containing about 4% lime and 0.2–0.5% sodium sulphide (which contains iron and turns the hides a bluish-green) for 7–21 days, with about 4 liftings. The object is to loosen the hair by softening the bottom layer of the epidermis. Mucins and mucoids are also dissolved out. The hair is then removed by a machine with a blunt knife, the hides are trimmed and the surplus flesh scraped off. The hair thus obtained finds use in plastering work and felt making, etc.

Skins are painted on the flesh side with a 2% sodium sulphide solution thickened with lime, de-wooled or unhaired the next day, trimmed, fleshed, well washed and limed further in a lime liquor containing arsenic sulphide.

The *first process* in the manufacture of glue is the liming and the quality of the product depends upon the thoroughness of this treatment. It is necessary to avoid hydrolysis of the collagen and the extent of this liming therefore depends upon the condition of the raw material, and with already limed stock reduced liming is usually desirable. For unlimed stock, saturated lime-water has been recommended, but in practice this has to be changed at frequent intervals. It is necessary to construct the whole plant so that it can be kept absolutely clean without excessive labour. It is best to employ several changes of a lime suspension in wooden or concrete vats using about 10% of lime on the weight of the stock, or less if caustic soda is used. The total time varies from 30–60 days, but is considerably less if caustic soda is present, and the stock is then firm and free from a greasy feel. If it is frequently turned over no bacterial action occurs. Bleaching agents, such as bleaching powder or sodium peroxide, and preservatives, such as phenolic compounds, are sometimes added, but may cause coagulation during evaporation.

The *second process* is carried out in the washing mills with running water until the washings are clear. As the removal of the lime is incomplete, acid is added to the next wash-water. The most commonly used are sulphurous and hydrochloric acids. The former has the advantage of being both a bleaching and antiseptic acid, but it has the disadvantage that appreciable

quantities of sulphur dioxide or sulphites may be left in the finished product. Commercial hydrochloric acid is used more frequently in the manufacture of glues where the presence of traces of iron or arsenic would not be considered as objectionable. After the acid treatment, the material must be in a nearly neutral condition with a  $p_H$  value of about 5.0. Stock containing rancid fats would yield turbid glue because of the emulsifying power of the oxidised acids. Such material can be improved by carbonation, that is blowing carbon dioxide through them in water until phenolphthalein is no longer reddened. In any case, the materials are then either used immediately or dried and stored ready for future use.

The *third process* is the extraction of the glue by "boiling" with a large quantity of water. The word "boiling" does not imply actual ebullition, but gentle cooking at a temperature of about 60°C. to convert the collagens into glue and allow the fat to rise without emulsifying with the gelatinous matter. This is the most important process of the manufacture, and the quality of the finished product depends upon a number of factors which are very difficult to control. It is necessary, for instance, to avoid as far as possible the formation of degradation products by prolonged heating. Very frequently, however, degradation products are present in certain portions of the skins, owing to overliming. These dissolve first, and the "first run" of glue is then of inferior quality compared with the second extraction.

Generally, the extraction of glue is carried out in open aluminium or wooden vats, 3 or 4 ft. deep and 6–8 ft. in diameter. Copper heating coils are placed at the bottom of the vats and covered with a perforated false bottom usually made of iron or copper. By this arrangement the materials do not come in contact with the coils, while the perforated false bottom is used as a support for a coarse filtering medium. The steam for heating comes from a vertical pipe in the centre surrounded by a wooden casing or "eye" passing through the false bottom so that when the liquor boils it rises through the casing and flows out at the top of the vat, passing down through the glue-stuff. For dry material, the vat is fitted with a "curb" in which the spatches can be piled and sink down gradually as they soften.

The vat is filled with the treated materials and enough water is allowed to run in to cover them, and steam passed through the coils, the temperature being maintained at about 60°C. (140°F.) for 6–8 hours or until a sample of the liquor forms a firm jelly on cooling. As much of the fat as possible is skimmed off and the glue liquor is then drawn off through a valve at the bottom of the vat, run into a tank, allowed to cool somewhat, and a further portion of fat allowed to separate.

More water is then added, and the "boiling" is continued until the necessary concentration has been reached. This second liquor will yield the best glue, but a large quantity will still be left in the hide stock, which is extracted by repeating the "boiling" 3 or 4 times, the temperature of the extracting water being increased if necessary.

The glue liquors must be filtered and concentrated, but as these processes are similar to those employed for bone glues they will be described later.

(b) **Bone Glue.**—For this purpose, bones of all kinds are used and vary, therefore, so much in composition that it is useless to give any detailed analysis. Apart from the marrow, blood-vessels, etc., they contain the main ingredients of the ash, calcium phosphate and carbonate, fat and the gelatin-forming substance ossein. The inorganic portion is so intimately blended and incorporated with the ossein that it is only by drastic treatment as, for instance, by the action of strong mineral acids, that they can be separated.

In many respects the processes used in the manufacture of bone glue differ from those described for hide glues. These differences do not refer to the extraction of the glue itself, but to the preliminary treatment of the raw material in order to obtain a number of very valuable by-products.

The ossein, the collagen of bones, may be isolated from degreased bones by a prolonged and somewhat expensive and troublesome treatment with dilute acids. The number of acids suitable for this purpose is limited, as some of them, *e.g.* nitric and acetic acids, have an injurious effect on the gelatin-yielding material. Hydrochloric acid is by far the most commonly used; the strength of the solution varies between 2 and 5%.

Ossein can be limed and treated in a manner similar to hides, but owing to the expense and the time required, this treatment is only used for the manufacture of gelatin.

In order to extract glue from untreated bones, the following process is adopted.

The green bones are first passed through a crusher, and then over a belt in order to remove by means of a magnet any metallic objects which may be present. In many cases the bones are thoroughly washed before crushing.

The crushed bones are then treated for the removal of fat. Fresh bones comprising the heads, ribs, shoulder-blades, etc., contain 12–13% while the large thigh bones ("marrows") yield 17–18%. Marine store bones, which have generally been used for making soups, Indian and South American bones rarely contain more than 12% of fat.

There are three methods of extracting fat from bones: (1) by heating the bones with water in a tank provided with a steam coil; (2) by heating with steam in a digester under pressure; (3) by extracting with a volatile solvent (*v.* BONE FAT).

By the first of these processes the yield of fat is small, but it is of good colour and finds ready use in many subsidiary industries such as soap-making.

The second process will extract more fat, but at the same time also a certain amount of the glue.

The solvent extraction process will remove practically the whole of the fat without injury to the glue-yielding material and is the one used in most modern factories. The usual solvents are benzine, benzol and trichlorethylene; benzene

was commonly used, but trichlorethylene and other modern solvents are rapidly taking its place owing to non-inflammability and lower cost of degreasing.

The idea that in order to obtain a good extraction of fat the bones must not contain more than 10% of moisture has been proved incorrect, as the presence of water will not hinder the extraction of the fat and will not cause loss of glue, especially if the solvent used has a low boiling-point, *e.g.* if trichlorethylene (b.p. 87°C.) is employed.

A modern fat-extracting plant consists generally of 6 cylindrical vertical extractors, each of a capacity of 5 or 10 tons, worked in sets of 3 units, one lot extracting while the other set is being emptied. The extractors are provided with wet and dry steam coils placed under a perforated false bottom.

After sorting, the crushed unscreened bones are filled into the extractors, the manholes are tightly closed, and sufficient solvent to cover them is allowed to run in from the storage tank. Steam is then admitted to the dry coils and the solvent is distilled over through a pipe placed at the top of each extractor and connected with suitable condensers often situated outside the building.

By formation of an azeotropic mixture the solvent carries off all the water contained in the bones; the mixture is passed, after condensation, into a separator which allows the solvent to be recovered and returned to the storage tank, and thence, automatically, to the extractor.

The heating is continued in this way until the condensed solvent is free, or practically free, from water, when extraction is assumed to be complete. The steam is then turned off, and the fat, together with the remaining solvent, is drawn off from the bottom of the extractor into a still for the recovery of the solvent.

The bones are then washed once or twice with the solvent, to remove from them as much as possible of the adhering fat. These washings are also drawn into the still, and high pressure steam from the wet steam coils is then blown into the extractors to completely expel all the solvent. This is continued until the condensate is all water, when the extractors are opened to admit a circulation of air for drying the bones. The whole operation takes about 12 hours.

The fat obtained by this method is, as a rule, highly coloured, and is known commercially as "benzine bone grease." It is freed from dirt, if necessary, by heating with hot water and settling, and is then run into barrels. It contains about 98% of fatty matter and is used for soap, candle, glycerin, and if made from fresh bones, for margarine making.

The bones are raked out, conveyed to a cleanser, consisting of a rotating cylindrical wire gauze sifter, where they are "polished" and all small particles of adhering tissues removed. The "polished" bones should be free from smell and not contain more than 0.25% of fat. In many works the extraction of the glue is carried out without subjecting them to any further preliminary treatment; in others they are subjected to maceration either in dilute alkali or

dilute acids. The acid treatment, for which dilute solutions of sulphurous acid are used, is supposed to facilitate the extraction of the glue, by causing a slight decalcification on the surface of the bone, while an alkaline treatment, either with milk of lime or dilute soda, has for its object the removal of substances which by their presence impair the properties of the glue. These substances occur always in the connective tissue of various organs, and belong to the chondroproteins; in the case of bones this chondroprotein is called osseo-mucoid and was isolated in notable quantities for the first time by Hawk and Gies (Amer. J. Physiol. 1901, 5, 388).

The extraction of glue from the "polished" bones is carried out in pressure tanks, commonly called "digesters." These are steel cylinders with convex ends, having a large manhole at the bottom for the removal of the spent material and a hinged lid for the charge.

Before the extraction, steam is blown through the bones in order to further clean them and to remove any trace of adhering solvent. When the digester is filled with steam, the steam outlet is closed and the pressure allowed to increase to the desired extent. Both the pressure and the time for which it is maintained vary in different works; in some, pressure and vacuum are applied alternately in order to ensure better penetration of the water and thus give more concentrated liquors.

When the pressure in the "digester" has been released, water preheated to 100–110°C. (212–230°F.) is run in to effect the extraction of the glue. As in the case of hide glues, several "runs" are made, each yielding glue of a different grade.

**TREATMENT OF GLUE LIQUORS.**—The liquors, either from hides or from bones, contain suspended fine materials. Several methods have been suggested for their elimination. In many works glue liquors are clarified by standing in tanks, kept warm by steam coils, here the dirt settles and the grease that comes to the surface is skimmed off. Not all glue liquors can be filtered bright; the protective action of the gelatin itself is a hindrance to a good filtration. Fuller's earth, charcoal and alumina have been recommended as filtering media, but the best results are obtained with cellulose. Cellulose, being slightly electronegative to water, holds the electropositive particles without adsorbing the glue, but in order to obtain a good filtration it is necessary to pack the cellulose loosely. Filter presses therefore prove to be useless and gravity filters should be used instead.

Many manufacturers prefer precipitating the suspended material by producing a colloidal coagulation in the glue liquor, which can collect and hold the suspended particles; albumin is added, for instance, to a comparatively cool liquor, and the temperature gradually raised until coagulation takes place. The liquor is then allowed to stand for the separation of the coagulum, and the clear portion siphoned off and filtered. Instead of albumin, blood is frequently used, or, in many cases, inorganic precipitants such as alum or acids which form insoluble salts with the alkaline earths.

The clarified glue liquors are then evaporated to the necessary concentration in vacuum pans, e.g. the Yaryan evaporator (v. Vol. IV, 409d).

Many glues have a strong tendency to foam when heated *in vacuo*; the addition of soaps (e.g. aluminum soap) or of tallow will, by altering the surface tension, decrease very markedly this tendency, but at the same time render the finished product useless for certain purposes.

After evaporation, the glue liquors before settling are bleached, if necessary, by treatment with sulphur dioxide, which is introduced through perforated pipes into the liquors contained in lead-lined tanks and kept liquid by steam coils. When the required shade has been reached, the liquors are ready for jellying and are run into wooden or galvanised iron troughs about 5 ft. long by 9 in. deep and 15 in. wide and allowed to cool. Great care is taken to keep these coolers free from putrefactive bacteria and they are frequently washed with sulphurous acid solution or fresh milk of lime. When set, the mass is removed and cut by a "wire knife" into sheets of suitable thickness, or the liquors may be run into shallow trays and the slabs cut to the required size. In modern practice many glues are prepared in the form of beads or flakes by running the glue liquor into a suitable liquid, and a preservative is generally incorporated.

The drying operation which follows requires very great care; artificial heat cannot be used, since the melting-point of the jelly is frequently not above 25°C. and in hot, and especially in thundery weather, it sometimes melts. Bacterial contamination often causes bubbles in the interior of the cakes. For these reasons the glue is often concentrated in the Yaryan or "Climbing Film" type of evaporator until it will set to a firm cake when run on to glass plates previously waxed or rubbed with ox-gall to prevent adhesion. Otherwise, the glue slices or "cakes" are laid out upon frames of galvanised wire and transferred to the drying tunnels, so constructed as to receive trucks each stacked with a number of frames.

The tunnels are of varying length, and air is blown through them in counter-current flow to the direction of the progress of the trucks. This exposes the first trucks carrying nearly dry glue to the driest air, while trucks with cakes from successive batches of glue and therefore only partially dry are exposed to cooler air practically saturated with water vapour. By this method the too rapid drying of the surface of the glue cake is avoided (case-hardening).

Steam coils and humidifiers are provided at the intake of the air duct and the temperature and relative humidity are carefully controlled by wet- and dry-bulb thermometers, or automatically in modern plant, throughout the drying; if possible, the air blown into the drying tunnels should be filtered, as even under the best conditions the amount of dust and accompanying bacteria deposited on the glue by the air-current is considerable.

A properly dried glue should contain from 12 to 18% of moisture. Many properties of the finished product depend on this hygroscopic moisture; a dehydrated glue has a low tensile



strength, while a damp glue has bad keeping qualities.

**Ossein.**—This is a preparation obtained by treating the fat-free bones with dilute mineral acids, when the phosphates, carbonates and soluble salts are removed. The residue consists of the glue-forming ingredients and is put on the market in a dry state for the manufacture of gelatin.

(c) **Fish Glue.**—The waste products of the fish industry give fish glue, which is the most important liquid glue. The raw materials are the skins (especially those of soles and plaice), the bladders of various fish and, chiefly, all varieties of fish offal. The quality of the glue prepared from ground fish such as cod, haddock, hake, etc., is higher and the yield is greater than in the case of glue made from most other fish, e.g. menhaden. Fish such as mackerel and herring contain large quantities of oil. The offal is carried by conveyors to a series of washing tanks placed overhead and thoroughly washed until the water contains a low percentage of chlorides. It then falls by gravitation into the digesters and is covered with water and heated with live steam. The length of the cooking varies with the nature of the glue stock. Usually the liquor formed by cooking the stock is drawn off when it becomes sufficiently concentrated and a second run of inferior glue liquor is obtained. The oil is skimmed off and 0.5–3.0% of preservative such as phenol, cresol or boric acid is added because bacterial growth would cause rapid decomposition. After straining, the liquors are evaporated to a uniform viscosity, and a sufficient quantity of some essential oil, dissolved in ethyl alcohol, is added to prevent mould-growth and to mask the fishy odour. Some fish glues are made opaque by means of a white pigment, such as zinc white, whilst others are bleached with sulphurous acid.

Fish glue is usually marketed as a liquid glue, which differs from hide and bone glues in consisting chiefly of proteoses and peptones and being soluble in water at 18°C. It is very adhesive but should not contain more than 0.2% of sodium chloride as otherwise it gives joints which will weaken in humid weather. It should be slightly acid to phenolphthalein. The best way of comparing different samples is to compare the times of drying and the hardness of the dried films produced in a room at 20°C. and 20% relative humidity.

**Isinglass.**—See under GELATIN.

**Glue Size** may be considered as a by-product, since it usually consists of the crude glue liquors which are the product of the third or fourth extraction of the raw material, and, if dried, would yield a glue of inferior quality.

Size is usually treated with sulphur dioxide to improve its colour and its keeping power. Zinc sulphate or boric acid is often added as a preservative, and when sold it usually contains about 25–38% of glue.

**Concentrated Size** consists of ground glue prepared from cakes of inferior shade and quality.

**Coloured or Opaque Glues** are made by the addition of a small quantity of some pigment, or finely ground chalk or whiting.

## CHEMISTRY AND PROPERTIES OF GLUE.

The products yielded by the hydrolysis of collagens may be divided into three groups:

(1) **Gelatin** (*q.v.*).—This is the first hydrolytic product. The commercial varieties are flexible and horny in the air-dry condition, when they contain 8–15% of water. When precipitated from alcohol or by salts, gelatin is pure white and nearly water-free. It is soluble in glacial acetic acid (such solutions being made use of in the familiar “Diamond Cement” and “Seccotine”). In cold water it swells to a transparent jelly which melts at temperatures from 30 to 40°C. giving a solution of gelatin which sets again on cooling if the concentration is above 1%. To avoid further hydrolysis in dissolving gelatin, the temperature must not exceed 50°C. and a solution heated above 70°C. will not return to its original state. The melting-point varies very considerably with the quality of the gelatin, but is little affected by concentration between 5 and 10%. A 10% jelly of best hard gelatin melts at about 38°C. but the melting point is raised by various salts, such as alum, chrome alum and basic chromium salts, which react with it chemically.

Commercial gelatins contain gelatoses and peptones, often in considerable quantities, and the protein chondrin is probably also present. Even the best French gelatin contains peptone. Bogue (“Chemistry and Technology of Gelatin and Glue,” New York, 1922, p. 28) gives the following percentages:

	Protein nitrogen.	Proteose nitrogen.	Peptone nitrogen.	Amino-acid nitrogen.
Russian isinglass.	91.0	4.4	4.5	0.1
Edible gelatin . .	87.8	11.3	0.7	0.2
Hide glue. . . .	84.6	12.4	2.6	0.4
“ . . . . .	52.0	38.6	8.4	0.9
Bone glue. . . .	73.5	16.4	8.1	2.0
“ . . . . .	31.5	50.6	14.8	3.0
Peptone . . . .	0.0	33.2	48.5	18.3

The chemical distinction between gelatin and glue is merely one of purity. Commercially a gelatin differs only from a glue in that the former is a very high grade product, is of high jelly strength, is light in colour, gives solutions that are reasonably clear and contains relatively less degradation products, see table.

Dry distillation of gelatin yields water and a dark thick oil, similar to Dippel's Oil, containing pyridine bases, aniline, etc. Formaldehyde, when added to gelatin in solution, solidifies it and renders it insoluble even in hot water. 8% of formaldehyde gives the maximum effect. This property has been utilised in waterproofing and in the production of the long extinct Vandura silk (*v. Vol. V, 1155*).

(2) **Chondrin** (*v. GELATIN, Vol. V, 509d*).—This horny substance, very similar to gelatin, is contained in most glues, but differs in being precipitated from its solutions by nearly all acids, though usually soluble in excess. It is

distinguished by giving, like mucin, a precipitate with acetic acid. It may be detected by adding a saturated solution of chrome alum to a 10% solution of the suspected gelatin, which will gelatinise while still hot if chondrin is present in injurious quantity. Many salts, such as alum, lead acetate and iron salts also precipitate it. Its gelatinising and adhesive powers are weaker than those of gelatin.

(3) **Mucin**.—This name covers a number of slimy substances, which swell, but do not dissolve in water. They are soluble in lime-water and are usually removed in the lining operation. They dissolve in 10% salt solutions, but are precipitated by more concentrated solutions. They are detected in glue by the addition of acetic acid which causes a precipitate. They are also thrown down by alum. If left in the glue, they give rise to "foaming," and have little or no adhesive or gelatinising properties.

**USES OF GLUE**.—A great variety of industries employ glue in some form or other, e.g. in sizing textiles, papers, walls, canvas, etc., and in book-binding. It is also largely employed in joiner's work, veneering, box-making, the making of matches, distempers, etc.

Mixed with glycerin, treacle or glucose it forms the compositions used as substitutes for rubber and for printing rollers, stamps, etc. Mixed with treacle or glycerin it is employed in making the familiar "jellygraph."

It is also used in photography, and as gelatin it forms part of the raw materials of cookery.

#### GLUE TESTING

The facts that commercial glue is not a pure substance and that traces of impurities materially affect its properties make its testing difficult.

The physical and chemical properties of glue depend on the nature of the raw material and on the methods of processing. It is not possible to draw up any simple tests which will evaluate completely the quality of a glue, or its suitability for a particular trade. If, however, the glue is made from a specific type of raw material by a standard method of manufacture, then the British Standard Methods for testing Joiners' Glues (British Standard No. 745—1937) and Bone, Skin and Fish Glues (British Standard, No. 647—1938) provide indications of the behaviour of the glue in use and may be taken as reliable criteria of quality. When more stringent specifications are required reference should be made to British Standards, Nos. 4 V 11, Dry Gelatine Glue; 5 V 10, Liquid and Jelly Gelatine Glues, Glues for Aircraft Purposes.

The relative importance of the tests to be employed depends very largely on the purposes for which the glue is intended. For veneering and general joiner's work, for book-binding and the like, a glue should have good joint-strength, little foam and good keeping qualities. It should also show a good jelly strength and be free from grease, or it may give uneven joints. The gummed paper and carton manufacturers are particularly interested in viscosity and foam, etc. The glue for use in the sizing of canvas and the like should show a good jelly strength and good tensile strength: foaming power and grease are of less importance. For preparing

distempers, the grease content should be low as it may give rise to flecks; the keeping power should be high, but the tensile strength and jelly strength are of less importance. It is not necessary in any particular case to employ all the tests. In practice the consumer usually knows from his experience the most suitable type of glue for his purpose. The problem then reduces itself to checking those properties which are relevant.

In testing glue the appearance should always be noted and the odour of a freshly prepared hot solution, which should not be objectionable. Jelly or liquid glues should be in the form of a jelly or viscous liquid, which, at the temperature stated by the maker, should, as supplied or after dilution with water, be of satisfactory consistency. The tests may be divided into two classes: physical tests upon some property, and chemical analysis for some constituent. The physical tests most commonly used are: (1) Jelly Strength, (2) Viscosity, (3) Melting-point, (4) Adhesive Strength, (5) Tensile Strength, (6) Keeping Quality, (7) Water Absorption, and (8) Foam Test. The chemical analysis includes the determination of the following: (1) Moisture Content, (2) Reaction ( $p_H$ ), (3) Grease, (4) Ash, (5) Chloride, and (6) Sulphur Dioxide.

The question of the sampling is one of prime importance. It is necessary to sample each container in a delivery if this consists of 5 or less. For larger deliveries of 6–50, 51–100, 101–500, and 501–1,000 the numbers are 5, 10, 15 and 20 respectively. The liquid sample is taken by a sampling tube, scoop or similar tool. Pieces are broken up or ground by hand in an iron mortar, and quartered to give a final 2 lb. sample.

(1) *Jelly Strength*.—As a general index to quality the jelly strength and/or viscosity are usually included. In testing the former, the glue solutions are arranged in order of merit by comparing the resiliency of their jellies as ascertained by the pressure of the finger tips. In the British Standard method, the sample is compared with an agreed standard sample under similar conditions. According to the grade of the powdered sample 5, 7.5 or 10 g. are weighed into a 150 c.c. beaker and 50 c.c. of cold distilled water added. The glue is allowed to soak until completely swollen, the beaker heated on a water-bath for 10 minutes during which the glue is all dissolved at not above 60°C. by constantly stirring. The glue liquor is poured immediately into a Chinese ointment-jar (internal measurements  $1\frac{1}{2}$  in.  $\times$   $2\frac{1}{2}$  in.) and the celluloid cap put on after 2 minutes. It is kept for 16 hours at 15°C. and the jelly is compared with that of the agreed sample by pressure with the finger.

The testing of the comparative consistencies of jellies by measuring their capacities for bearing weights was originally suggested by Lipowitz (Neue Chem.-Tech. Unters. Berlin, 1861, 37). His scheme has formed the basis of many methods proposed from time to time; amongst them those suggested by E. S. Smith (U.S.P. 911277) and by Alexander (U.S.P. 882731) may be mentioned as they tend to overcome the

error which always attends the breaking or compression of a jelly, due to the formation of a "skin" at the surface.

Sheppard, Sweet and Scott (Ind. Eng. Chem. 1920, 12, 1007; J. Amer. Chem. Soc. 1921, 43, 539) at the laboratories of the Eastman Kodak Co. have developed an apparatus in which cylinders of gelatin jelly are submitted to torsional stress. This method is scientific and capable of giving absolute results, but has not been adopted in industrial practice.

Another method, whereby reliable comparative results may be obtained, consists in determining the jelly strength by means of a balance provided with a pan at one end of the beam and a counterpoise at the other. At the bottom of the pan is soldered a rod on which is fixed a steel ball of standard diameter. The glue jelly is prepared by weighing 1.5 g. of the glue to be tested in a small glass cylinder (10–15 mm. diameter) graduated to 15 c.c. at 15°C. Water is added and the glue allowed to soak overnight. The volume is then made up to 15 c.c., the glass cylinder gradually warmed on a water-bath, and the contents stirred until all the glue goes into solution. A few drops of toluene are added to prevent the formation of a "skin" and the solution is allowed to cool slowly. The cylinder is then placed in a cold chamber the temperature of which should not go below 1° or 2°C. After the lapse of 3 or 4 hours the cylinder is placed under the plunger and the balance adjusted to zero by means of the counterpoise, while the steel ball just touches the jelly. The height of the plunger can be adjusted if necessary. Weights are then slowly added to the pan until a pointer has indicated an arbitrarily fixed deflection. A comparison is made with a jelly prepared at the same time with purified gelatin or an accepted standard glue.

Where there is no agreed sample glue for comparison the B.S.I. have adopted the Bloom jelly strength tester (Ind. Eng. Chem. [Anal.], 1930, 2, 34; British Standard No. 647—1938). An extra-wide-mouthed test bottle is used of 155 c.c. capacity, 59 mm. internal diameter and 66 mm. outside diameter and 85 mm. height overall. A tapered rubber stopper with a base diameter of 42–45 mm. is cut in half and the upper portion centrally perforated by means of a red hot 2.5 cm. brad. The upper half of the stopper is used to obtain a snug fit in the neck of the bottle and the air vent prevents the stopper from being blown out during the melting and heating of the sample. 15 g. of the sample are put in the test bottle and 105 c.c. of distilled water at 15°C. added whilst stirring. It is allowed to soak overnight at 10–15°C. The bottle is placed for a few minutes in water at 20–30°C. to prevent cracking before putting it into the melting bath below 70°C., where it is brought to 62°C. in less than 15 minutes. After closing the bottle with the stopper, now carrying a thermometer, and before reaching 62°C., the solution is made uniform by swirling the bottle. The bottle is then kept at 10±1°C. for 16–18 hours. The determination of jelly strength made with the Bloom gelometer, adjusted to give a 4 mm. depression and to deliver shot at the rate of 200 g. per 5 seconds. The results are

expressed in grams required to produce the 4 mm. depression.

(2) *Viscosity*.—This has always been considered, by both manufacturers and users, as an important test in the evaluation of a gelatin or glue. In the British Standard method, 105 c.c. of cold, distilled water are added to 15 g. of the glue in a corked flask. After standing 2 hours, it is placed for 10 minutes in a water-bath at 35°C., dissolution being aided by gentle stirring. The flask is cooled to 40°C. and placed in a thermostat at 40±1°C. for  $\frac{1}{2}$  hour. The liquid is then poured through a funnel, loosely plugged with cotton wool, into a British Standard U-Tube Viscometer (B.S. 188—1937) and allowed to stand for  $\frac{1}{2}$  hour before taking the measurement. It is essential that the time of efflux should be within the accurate range of the instrument chosen, which will be usually No. 2 or No. 3, and that the instructions given in the Specification be adhered to. In making up a solution, and in order to obtain comparable results, the percentage of moisture contained in the sample must be taken into consideration. The percentage composition of the solution should always refer to the dry weight of glue. The results are expressed as the viscosity in centipoises of the glue at a concentration of 12.5% by weight and a temperature of 40°C.

The viscosity of a gelatin (or glue) solution varies with keeping: the change in viscosity which takes place when a gelatin solution is kept at a lower temperature after being heated for a short time at 100° is shown by the following figures (water 1):

Viscosity at	After heating for .				
	5 mins.	10 mins.	15 mins.	30 mins.	60 mins.
21° . .	1.83	2.10	2.45	4.13	13.76
24.8° . .	1.65	1.69	1.74	1.80	1.30
31° . .	1.41	1.41	1.42	1.43	1.42

If the heating is prolonged, as would be the case in commercial practice, the viscosity reaches a minimum and constant value. This is due to an irreversible change, that is, to a decomposition of the gelatin.

It follows that the temperature at which the viscosity of a gelatin solution is determined is of very great importance. Von Schroeder, in his important work on the viscosity of gelatin solutions (Z. physikal. Chem. 1903, 45, 75), showed that at a temperature of 31°C. (see table) the viscosity does not alter over a period of 1 hour, thus indicating the approach to some kind of equilibrium. C. R. Smith (J. Amer. Chem. Soc. 1919, 41, 135) and, later, Bogue (*ibid.* 1922, 44, 1313) found that at a temperature of 32–35° the gel form could not exist, and that no evidence of plastic flow could be observed above this temperature, which should therefore be used for viscosity readings of a 10% gelatin (or glue) solution.

(3) *Melting-Point*.—The melting-point of a glue is intimately correlated with its jelly strength and viscosity. It depends upon the

percentages of pure gelatin and gelatin degradation products it contains. The greater the concentration of gelatin the higher will be the melting-point; the greater the amount of degradation products the lower will be the value found.

Many methods have been suggested for the measurement of the melting point, but most of them will only give approximate results. The method described by Cambon (J.S.C.I. 1907, 26, 703) has been used in the British Standard No. 647, 1938. The apparatus consists of a brass bowl 22 mm. in height, 17 mm. external diameter at the top and 15 mm. at the bottom. It should weigh exactly 7 g. Into this fits loosely a glass rod 40 mm. long and 3 mm. in diameter, which is flattened at one end to a disc of 9 mm. diameter and fashioned at the other end into a hook. 15 g. of the powdered sample are placed in a beaker with 105 c.c. of cold, distilled water, allowed to stand for 2 hours, placed on a water-bath and maintained at 50°C. for 10 minutes, dissolution being aided by gentle stirring. The glue liquor is then poured into the bowl, the rod inserted to the base of the bowl and maintained in an upright position for 16 hours in a thermostat at 10°C. The cup is then totally immersed and suspended by the glass rod in a beaker of water at 15°C. placed in a water-bath at 20°C. The water in the latter is heated so that the temperature of the water in the beaker rises at the rate of exactly  $\frac{1}{4}$ °C. per minute. The temperature of the water in the beaker at which the bowl falls from the rod is taken as the melting-point.

References to other methods which have been suggested are Chercheffski's (Chem.-Ztg. 1901, 25, 413); Kissling's (Z. angew. Chem. 1903, 17, 398); Smith's (J. Amer. Chem. Soc. 1919, 41, 146); and the one described by Sheppard and Sweet (Ind. Eng. Chem. 1921, 13, 423), which is very accurate, but necessitates the use of a complicated apparatus. The Aeronautical Inspection Directorate, however, have suggested another method, which is simpler and equally accurate. A 20% glue solution is poured into a U-tube, which is then placed in cold water to allow the glue or gelatin to set properly. One end of the U-tube is connected through a T-piece to a gauge and suitable means to obtain a pressure head of 6 in. of water, the connections being air-tight. The U-tube is then immersed in a beaker of water which is heated gradually by means of a micro-burner. The temperature at which the glue melts is indicated by the fall of the meniscus in the pressure gauge.

(4) *Adhesive Strength*.—If a glue has to be used as a binding agent in joint or veneer work, the main test is its adhesive strength.

This property of glues has been studied extensively by Douglas and Pettifor on behalf of the Adhesives Research Committee and their valuable work is summarised in Appendix I of the Third Report of the Committee (H.M.S.O. 1932). They recommend the use of the simple lap joint, already suggested in 1916 by the Aeronautical Inspection Directorate, and give the procedure to be followed in order to obtain the minimum of variation in the test results. Their work leads to the conclusion that the strength of a common

glued wood joint depends upon two factors: (1) Mechanical embedding, and (2) Specific adhesion. Of these the greater emphasis should be laid on (1). The British Standard defines joint strength in shear as the load required to break a walnut overlap joint, when determined by the specified method. This value should not be less than 1,000 lb. per sq. in. for joiner's glues whether cake, powder, liquid or jelly. For the determination, the glue liquor is prepared by soaking 10 g. of the sample in 15 c.c. of cold, distilled water in a beaker for 2 hours and melting on a water-bath for 10 minutes at not above 60°C. Liquid and jelly glues are tested at the original concentration. The test pieces are made from two slips of carefully selected, straight-grained, dry, black American walnut and are  $4\frac{1}{2}$  in.  $\times$   $\frac{3}{8}$  in.  $\times$  1 in. The 1 in. face must lie in a tangential direction to the grain and the  $4\frac{1}{2}$  in. length must be approximately parallel to the longitudinal direction, but shall preferably make a small angle of 3° with the grain. The two parts of the test-piece are assembled so that the grain tends to run through the joint from one piece of wood to the other. The overlapping surfaces are toothed by hand with a sharp, fine toothing-plane having 20–25 teeth per inch. The glue is applied with the finger, avoiding air bubbles, to one surface of each of two test slips at ordinary air temperature, which must not be below 10°C. When the surface of the glue has become tacky, the surfaces are placed together without rubbing, so as to produce a 1 in. overlap joint. Six of these test-pieces are made. They are clamped immediately after closure of the joint in a suitable press under a pressure of 200 lb. per sq. in. for 16–20 hours, and are then conditioned at 12–24°C. at 50–75% R.H. for 72 hours. The pieces are put into an approved testing machine with the grips 4 in. apart and arranged so that the load is applied in the plane of the unstrained joint. The load is applied uniformly at the rate of about 1,500 lb. per minute. The total load required to break a joint is regarded as the strength of the joint and the average of six is taken, an experimental error of 5% being allowable in the mean figure.

(5) *Tensile Strength*.—It has been shown by McBain and Hopkins (Second Report Adhesives Research Committee) that it is possible to obtain a measure of the strength of the glue itself by tensile strength measurements and to study other properties such as adaptation to volume change consequent upon setting, shrinking, ability to withstand impact or actual bending, the effect of humidity, etc.

Uniform glue films are obtained (Lee, Ind. Eng. Chem. 1930, 22, 778) by pouring the necessary amount of a 20 or 30% glue solution on a highly polished Bakelite plate accurately levelled. The film, when dry, can be easily removed and cut into the required shape of test-piece. McBain and Hopkins (*l.c.*) state that it is necessary to rehumidify the film before cutting in order to prevent it from splitting. The approved type of test-piece consists of a straight strip, the long sides of which can be cut with one stroke of the scissors, thereby minimising the possibility of snipping the edges. The ends of the test-piece are reinforced with paper and fixed in the grips

of a Schopper dynamometer of the pendulum type. The grips are supported on a horizontal knife edge, and the load is applied uniformly and at a rate which can be determined.

The test strip should be bent backwards and forwards several times before the tensile strength is measured, and the result compared with that of another test strip which has not been subjected to previous bending.

(6) *Keeping Quality*.—This is intended simply as an index of the behaviour of the glue in practice and is not to be taken as a substitute for a more complete bacteriological examination. The cake or powdered varieties of joiner's glues should retain their properties for at least 12 months when stored in a cool, dry place. The period with jelly or liquid glues is agreed on by the purchaser and vendor. In the British Standard method of determination, 5 g. of the powdered sample are soaked in 20 c.c. of cold distilled water until completely swollen. It is then heated on a water-bath until dissolution is completed, and transferred to a B.S. Petri Dish (B.S. 611), 94 mm. diameter. It is covered and placed in an incubator maintained at 40°C., taken out after each 24 hours and cooled for inspection. The periods are noted when liquefaction, putrefaction or moulds occur.

(7) *Water Absorption*.—The behaviour of glue when immersed in water at 18–20°C. for 24 hours is a useful criterion of its quality. Generally speaking, the greater the water absorption the better the glue, provided that the cake does not break and remains firm. Fine bone and skin glues increase in weight about 8–11 times, common glues about 5 times, but a bad glue will pass entirely into solution. In the British Standard Specification, water absorption is defined as the proportion of water absorbed by a powder retained on a  $\frac{1}{16}$  in. B.S. test sieve and passing through a  $\frac{1}{8}$  in. B.S. sieve. 10 g. of the powder are weighed into a 300 c.c. squat beaker containing 100 c.c. cold distilled water. It is kept for 16 hours at 10°C. with occasional stirring. The supernatant water is then poured off through a funnel fitted with a strainer of stretched damp muslin of about  $\frac{1}{16}$  in. mesh. The quantity of water passing through the funnel in 5 minutes is measured. The difference between this figure and 100 is the water absorbed by 10 g. of the glue.

(8) *Foam Determination*.—The peptones present in glue increase its tendency to foam and this test is of interest when the glue is to be applied by special machines. In the British Standard method for foam determination, 5 g. of the powdered sample are allowed to soak in 50 c.c. of cold distilled water in a beaker until completely swollen. The beaker is heated in a water-bath to not above 60°C. until dissolution is completed. 50 c.c. is poured into a 100 c.c. stoppered cylinder (diameter 32 mm.  $\pm$  2 mm.) The internal height to graduation mark is 15  $\pm$  0.5 cm. and to the shoulder is 23  $\pm$  0.5 cm., and the air space above the graduations corresponds to 50 c.c.  $\pm$  2 c.c. This is placed in a water-bath at 45°C. for 1 hour. The cylinder is then shaken vigorously with a throw of about 12 in. at a rate of 3 shakes per second for 1 minute. It is replaced in the water-bath at

45°C. and left until the height of the liquor corresponds to 45 c.c. The time taken for this 45 c.c. meniscus to form and the volume in c.c. of the foam above the liquid are reported.

*Chemical Analysis*.—The following points and further determinations may be added to those described under GELATIN (*q.v.*).

(1) *Moisture Content*.—Glues contain 12–18%, and a figure of 18% is the limit with cake or powder joiner's glues. A very low result is not desirable, as it shows that the glue has been over-dried and has little tenacity, while a high result throws doubt on its keeping quality.

(2) *Reaction* ( $p_H$ ).—This should be from 5.0 to 8.5 for cake or powder glues and between 4.0 and 8.0 for jelly or liquid glues. Free acid can be determined directly by titrating to phenolphthalein.

(3) *Grease*.—Only a negligible amount should be present.

(4) *Ash*.—The ash content of good glues varies from 1.5 to 3.0%. Some bone glues contain considerable quantities of calcium phosphate, while hide glues are apt to contain calcium sulphate or chloride resulting from the neutralisation of the lime used in preparing the stock, and are frequently alkaline, due to the presence of lime. Various whitening agents, such as zinc oxide, lead sulphate or carbonate, chalk, clay, etc., may be present. Glues weighted with barytes, etc., and some coloured glues also yield high ash weights.

(5) *Chloride*.—The chloride content is one index of the behaviour under various atmospheric conditions. It should not exceed 2% (as NaCl) in joiner's solid glues. 5 g. of the powdered sample are weighed into a nickel or platinum basin and 10 c.c. of cold, distilled water added. After soaking for 1 hour, it is heated on a water-bath until dissolved and 5 g. of pure lime added. After drying on a steam-bath and ignition so that the sample is completely ashed, the residue is extracted by boiling rapidly with small quantities of water and the salt determined by neutralising with acetic acid and titrating with  $N/10$   $AgNO_3$ .

(6) *Sulphur Dioxide*.—This is important when the glue is being used for sizing coloured paper, textiles or artificial silk. 27.5 g. of the powdered sample are weighed into a 1-litre round-bottomed distillation flask. 300 c.c. of distilled water containing 5 g. of phosphoric acid ( $d$  1.7) are added and the flask is connected by a bent glass tube fitted with 2 bulbs to a glass condenser, to the exit of which a "B.A.R." bubbler is fixed. 25 c.c. of  $N/2$  iodine solution are placed in a receiving flask. Pure  $CO_2$  is bubbled through the contents of the distillation flask throughout the determination. The distillation flask is surrounded by a water-bath and heated until the glue is dissolved. The flask is then heated directly until 200 c.c. of distillate have been collected. The distillate is acidified with 5 c.c. conc.  $HCl$ , evaporated to 75 c.c. and filtered. The filtered solution is heated to boiling, 10 c.c. of 0.5  $N$   $BaCl_2$  solution added slowly and allowed to stand overnight. It is then filtered through an ashless filter-paper, which is washed with hot distilled water and ashed. The percentage  $SO_2$  is calculated from the weight of barium

sulphate. Blank determinations should be made on the chemicals used with the rubber stoppers and  $\text{CO}_2$  apparatus.

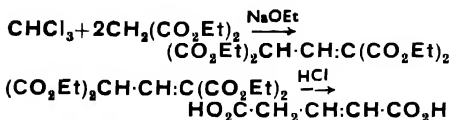
(7) *Gelatin*.—Many tests have been devised for determining the gelatin contents of glues, such as precipitation with zinc sulphate and estimating the nitrogen in the precipitate, precipitation with tannic acid, etc., but they are all untrustworthy. Possibly the formaldehyde titration (*see* GELATIN, Vol. V, 507a) gives the most reliable information.

**Bibliography.**—Lambert, "Glue, Gelatine and their Allied Products," London, 1905; Fernbach, "Glues and Gelatine," New York, 1907; Rideal, "Glue and Glue Testing," London, 1914; Reports of Adhesives Research Committee, London, 1922-32; Bogue, "Chemistry and Technology of Gelatine and Glue," New York, 1922; Thiele, "Leim und Gelatine," Leipzig, 1922; Procter, "Principles of Leather Manufacture," 2nd ed. London, 1922; Alexander, "Glue and Gelatine," New York, 1923; Sheppard, "Gelatine in Photography," New York, 1923; Cambon, "Fabrication des colles et gélatines," Paris, 1923; Gerngross und Goebel, "Chemie und Technologie der Leim- und Gelatine-fabrikation," Dresden and Leipzig, 1931; Stadlinger, "Die Leimfibel," Berlin, 1929; Sauer, "Leim und Gelatine," Steinkopff, 1927; Smith, "Glue and Gelatine," London, 1929.

Extensive bibliographies on glue are given by R. Dittmar (Kolloid-Z. 1906, 1, 80), R. H. Bogue (Chem. Met. Eng. 1920, 23, No. 5), and W. Simon (*ibid.* 1938, 84, 101).

"GLUSIDE" (v. Vol. IV, 28d).

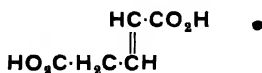
**GLUTACONIC ACID.** Propene- $\alpha$ -dicarboxylic acid,  $\text{HO}_2\text{C}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is best prepared by one of two methods. In the first of them, due to Conrad and Guthzeit (Annalen, 1883, 222, 249), chloroform is condensed with ethyl disodiummalonate and the resulting yellow sodium compound decomposed with dilute hydrochloric acid, yielding ethyl  $\alpha$ -dicarbethoxyglutaconate, which is then hydrolysed and decarboxylated to glutaconic acid by means of strong hydrochloric acid:



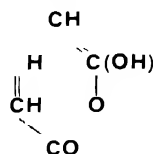
In the second, more recent, method (Grundmann, Ber. 1937, 70 [B], 1148) oxalocrotonic acid (readily obtained by hydrolysis of the condensation product of ethyl oxalate and ethyl crotonate) is oxidised with warm 3% hydrogen peroxide:



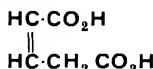
The acid obtained by both of these methods has m.p. 138° and is now known to be the *trans*-acid:



This acid, on treatment with acetyl chloride, yields, not a normal anhydride, but the hydroxy-anhydride (m.p. 87-88°):



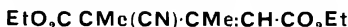
hydrolysis of which, under ordinary conditions, yields only the *trans*-acid. Malachowski, however (*ibid.* 1929, 62 [B], 1323) succeeded in preparing the *cis*-acid,



by very careful hydrolysis of the hydroxy-anhydride. The *cis*-acid, so obtained, melts at 136°, but shows a considerable depression on admixture with the *trans*-acid and also differs from the latter in the rate with which it undergoes isotopic exchange with deuterium oxide (Evans, Rydon and Briscoe, J.C.S. 1939, 1673); there is thus no doubt of the reality of the two stereoisomeric forms.

**Isomerism of the Glutaconic Acids.**—The elucidation of the isomerism phenomena displayed by glutaconic acid and its alkyl derivatives has played a great part in the development of modern views on tautomerism.

Rogerson and Thorpe (*ibid.* 1905, 87, 1669, 1685) showed that the *two* distinct esters



and



gave, on hydrolysis, the *same* dimethylglutaconic acid. This they interpreted as proving the identity of the two possible acids:



and

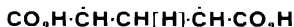


A similar identity was found in the cases of  $\alpha$ - and  $\gamma$ -methyl- and the  $\alpha$ -methyl- $\gamma$ -ethyl- and  $\alpha$ -ethyl- $\gamma$ -methyl-glutaconic acids. These observations were taken to imply the equivalence of the  $\alpha$ - and  $\gamma$ -positions in glutaconic acid (*cf.* the equivalence of the two *o*-positions in a mono-substituted benzene derivative).

In addition to this peculiarity, the glutaconic acids showed other anomalous properties, viz. no stereoisomeric forms were known (in 1905), geometrical isomers having been sought for without success; they also showed anomalous addition reactions, and they formed hydroxy-anhydrides instead of normal anhydrides. These anomalies were found to disappear completely when the mobile hydrogen atom was locked by substitution, e.g. in



Thorpe himself (J.C.S. 1923, 123, 3343) expressed his point of view as follows: "All experiments on the glutamic acids . . . combine to show that there is something in the constitution of these substances which conventional symbols do not explain, and that this 'something' is connected with the mobile hydrogen atom of the system, because it disappears when that atom is absent; we assume, therefore, that this structural peculiarity is connected with the mode of attachment of the mobile hydrogen atom to the rest of the molecule." On the basis of such reasoning Thorpe, in 1905, put forward his well-known "normal" formula:



Feist (Annalen, 1909, 370, 41) had prepared a second, labile, form of  $\alpha$ -methylglutaconic acid which he regarded as a stereoisomeride of the stable acid. Thorpe, however, was of opinion that the stable acid possesses the "normal" structure while Feist's and the other labile acids which were later isolated have the conventional unsaturated structure:



In 1931, McCombes, Packer and Thorpe (J.C.S. 1931, 547; cf. Bull. Fitzgerald, Packer and Thorpe, *ibid.* 1934, 1653) succeeded in resolving the stable form of  $\alpha$ -dimethylglutaconic acid; thus showing that this acid has the "unsaturated" structure B, which contains the essential asymmetric carbon atom, absent in the "normal" structure A:

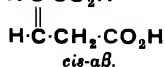


"Normal."  
A.



"Unsaturated."  
B.

A reinvestigation of the whole subject was undertaken by Kon and collaborators, working in Thorpe's laboratories at South Kensington (Kon and Nanji, *ibid.* 1931, 560; 1932, 2426, 2557; Kon and Watson, *ibid.* 1932, 1, 2434; Gidvani, Kon and Wright, *ibid.*, p. 1027; Gidvani and Kon, *ibid.*, p. 2443). This fresh attack was much benefited by the experience gained in the work on three-carbon tautomerism which had been carried out at South Kensington in the nineteen-twenties. It may now be concluded, as a result of these investigations, that the isomerism of the glutamic acids and their derivatives is due to the simultaneous occurrence of three-carbon tautomerism and *cis-trans* isomerism. On this view it will be seen that an unsymmetrically substituted glutamic acid can give rise to four isomers, e.g.:



*cis*- $\alpha\beta$ .



*cis*- $\beta\gamma$ .



*trans*- $\alpha\beta$ .



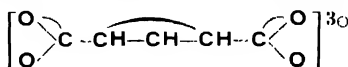
*trans*- $\beta\gamma$ .

Usually only two forms are encountered in practice, viz. the *cis*- $\alpha\beta$  and the *trans*- $\beta\gamma$  isomers, but Kon and Watson (*l.c.*) were able to prepare all the four possible  $\alpha$ -benzyl- $\beta$ -methylglutaconic esters and three out of the four possible corresponding acids. The absence of anomalous behaviour in glutamic acid derivatives with no mobile hydrogen atom also receives an explanation, since such compounds will show only normal *cis-trans* isomerism, three-carbon tautomerism being structurally impossible in such compounds. The following articles should be consulted for further information on this subject: Thorpe, *ibid.* 1931, 611; Kon, Annual Reports, 1932, 29, 140; instead, J.C.S. 1941, 457.

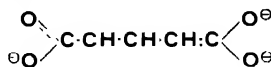
It is evident that the tautomerism of glutamic acid itself



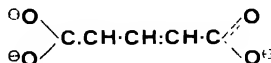
is not susceptible of study by ordinary means. Nevertheless an estimate of the very high mobility of this "crypto-tautomeric" system has been made by Evans, Ryder and Briscoe (*l.c.*) by a study of the exchange reaction between glutamic acid and deuterium oxide. These authors point out that the isomerisation takes place through a common mesomeric ion:



which is a resonance hybrid of the two possible canonical structures:



and



This common mesomeric ion is, in fact, the modern successor of Thorpe's "normal" formula. There can be little doubt that the resonance energy set free in the formation of this ion is responsible for the "reversion to type" which was another puzzling feature of the earlier work on the chemistry of the glutamic acids (cf. Ingold, Oliver and Thorpe, *ibid.* 1924, 125, 2128).

H. N. R.

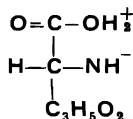
**GLUTAMIC ACID,  $\alpha$ -Aminoglutaric Acid,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$** , was discovered by Ritthausen in 1866 (J. pr. Chem. 1866, [i], 99, 6, 454) among the products of the hydrolysis of wheat gluten by sulphuric acid, and hence called by him *glutaminic acid*. Subsequently, Ritthausen and Kreusler (*ibid.* 1871, [ii], 3, 214), Gorup-Besanez (Ber. 1877, 10, 780), Schulze (Z. physiol. Chem. 1892, 9, 253) and Wroblewski (Ber. 1898, 31, 3218) showed that it was formed by the hydrolysis of other vegetable proteins; and Hlasiwetz and Habermann (J. pr. Chem. 1873, [ii], 7, 397), Panzer (Z. physiol. Chem. 1897, 24, 138), Abderhalden and Fuchs (*ibid.* 1908, 57, 339) isolated it from

the products of hydrolysis of animal proteins. It has been found in blood (Abderhalden, *ibid.*, 1913, **88**, 478); in tomato molasses (Monti, Chem. Zentr. 1912, I, 501); in molasses (Stoltzenberg, Ber. 1913, **46**, 557); in echinoderm (Edlbacher, Z. physiol. Chem. 1915, **94**, 264); in yeast (Meisenheimer, Chem. Zentr. 1915, II, 1259); in certain brown seaweeds as an octapeptide (Haas and Hill, Biochem. J., 1931, **25**, 1472); and among the products of hydrolysis of crystalline insulin (Jensen and Wintersteiner, J. Biol. Chem. 1932, **97**, 93), of certain seaweeds (Schindelmesser, B.P. 481898), of beef fibrin (Bodensky, J. Biol. Chem. 1936, **115**, 101) and of the protein of silk-worm chrysalis (Pan and Sun, Chem. Ind. China, 1936, **11**, No. 2, 1). For the glutamic acid content of various proteins, see Jones and Mocler (J. Biol. Chem. 1928, **79**, 429), also Fürth (Scientia Pharm. 1934, **5**, 21). *d*-Glutamic acid is formed from *L*-histidine by the action of liver histidase (Abderhalden and Hanson, Fermentforsch. 1937, **15**, 274), and probably from proline in kidney (Weil-Malherbe and Krebs, Biochem. J. 1935, **29**, 2077).

Glutamic acid is ordinarily prepared and manufactured by hydrolysis of casein or molasses and of vegetable proteins such as gluten, usually with hydrochloric acid or sulphuric acid (U.S.P. 1928840), but alkali (3–7% as sodium hydroxide) has been used (B.P. 385054; U.S.P. 1947563). In the literature there are many descriptions and numerous patents for the use of hydrochloric acid for this hydrolysis, most of them differing only in details such as the concentration of the acid, the time and temperature of heating, the use or omission of preliminary digestion, etc. The effects of these variables on the yield from soya-bean protein have been studied systematically by Tseng and Chu (Sci. Quart. Nat. Univ. Peking, 1932, **3**, 53; A. 1933, 814) and by Rokusho, Tanaka and Saito (J. Agric. Chem. Soc. Japan, 1937, **13**, 916). Bartow describes an autoclave for the hydrolysis of gluten or molasses in which the reaction can be conducted under pressure (Chem. Zentr. 1936, II, 246). The addition of ferric chloride, tin, nickel, lead or copper as catalysts to assist hydrolysis of gluten is recommended by Cheng and Adolph (J. Chinese Chem. Soc. 1934, **2**, 221); small amounts of nitric acid or manganese dioxide have also been specified (U.S.P. 1890590). Kumagai suggests the use of chlorine water containing 1% magnesium chloride in place of hydrochloric acid (U.S.P. 2050491). A preliminary separation of zein by aqueous-alcoholic extraction of gluten press-cakes, followed by precipitation with water, has been suggested (U.S.P. 1992804). For reviews covering the preparation of glutamic acid by the hydrolysis of gluten, see Tseng and Hu (J. Chinese Chem. Soc., 1935, **3**, 154) and Sato and Tsuchiya (J. Taihoku Soc. Agric. Forestry, 1936, **1**, 79). The product obtained in these preparations is usually freed from the salts of betaine, and the alkali metals (B.P. 265831; U.S.P. 1928840), by adding HCl and concentrating below 50°, the impurities are separated, and the mother liquor heated to 80° when glutamic acid hydrochloride crystallises on cooling. The free acid can be recovered from the hydrochloride by care-

ful neutralisation with alkali (carbonate or hydroxide), or, if racemisation is to be avoided, by aniline (King, Organic Syntheses Coll., Vol. I, 281) or *N*-alkylglycines, e.g. sarcosine or betaine (U.S.P. 1976097). Kutscher (Z. physiol. Chem. 1899, **28**, 123) isolated glutamic acid from the products of hydrolysis of casein by sulphuric acid, by precipitating the larger part of the organic bases with phosphotungstic acid, and removing the excess of sulphuric acid and phosphotungstic acid from the filtrate by means of barium hydroxide; the leucine and tyrosine crystallised out of the filtrate, and from the mother liquor the aspartic and glutamic acids were separated through their copper salts, that of glutamic acid being more soluble. Glutamic acid may be prepared from its hydrochloride by passing ammonia through the solution and evaporating to dryness; the greater part of the acid may be separated by fractional crystallisation and the remainder precipitated by alcohol (Abderhalden, Z. physiol. Chem. 1912, **77**, 75). Andrlík (Z. Zuckerind. Bohm. 1915, **39**, 387) obtained the acid from aqueous solution by means of tartaric, sulphuric or phosphoric acid. Siegfried and Schutt (Z. physiol. Chem. 1912, **81**, 261) prepared the acid by way of the insoluble normal barium salt. For the application of electro-osmosis to the separation of glutamic acid, see Ikeda and Suzuki (U.S.P. 1015891); Scheermesser (Pharm. Ztg. 1915, **60**, 487); Corti (J.S.C.I. 1917, **36**, 979; B.P. 106081); U.S.P. 1986920 and G.P. 652765.

The identification of glutamic acid is possible by the preparation of the 3:5-dinitrobenzoyl derivative (Saunders, Biochem. J. 1934, **28**, 580) or by oxidative deamination with surviving guinea-pig kidney sections into  $\alpha$ -ketoglutaric acid, which is isolated and identified as the 2:4-dinitrophenylhydrazone (Edlbacher and Neber, Z. physiol. Chem. 1934, **224**, 261). Glutamic acid and other acyclic amino-acids neutralised with sodium carbonate, give a deep red colour when added to uric acid which has been heated with nitric acid (Arreguine, Semana med. Buenos Aires, 1930, **37**, 1074; Amer. Chem. Abstr. 1930, **24**, 3488). For its quantitative estimation in the products of protein hydrolysis, see Foreman (Biochem. J. 1914, **8**, 465), and for the determination by formal titration using litmus paper as indicator, see Buogo (Annali Chim. Appl. 1934, **24**, 79). For the determination by potentiometric titration, see Balson, Earwicker and Lawson (Biochem. J. 1935, **29**, 2700). Although the structure given at the head of this article explains the chemical behaviour of glutamic acid, there is evidence that in solution it exists in a Zwitterion form;



for example, the exchange reaction with HDO (Ogawa, Bull. Chem. Soc. Japan, 1936, **11**, 367) and the formation and behaviour of complexes with iron (Smythe and Schmidt, J. Biol. Chem. 1930, **88**, 241). For the activity coefficients in



aqueous solution, *see* Hoskins, Randall and Schmidt (*ibid.* 1930, **88**, 215; *cf.* Miyamoto and Schmidt, *ibid.* 1931, **90**, 165); for the dielectric constant in aqueous solution, *see* Devoto (Gazzetta, 1932, **61**, 897); and for the infra-red absorption spectrum, *see* Heintz (Arch. phys. biol. 1937, **14**, 131). Glutamic acid is asymmetric and exists in *d*-, *l*- and *dl*-forms. Lutz and Jirgensons (Ber. 1930, **63** [B], 448) describe a graphical method of assigning optically active  $\alpha$ -amino-acids to the *d*- or *l*-series. The rotatory power of the optically active forms is a function of the  $p_H$  of the solution (Vellinger, Compt. rend. 1932, **194**, 718).

***d*-Glutamic Acid**, the naturally occurring compound, crystallises from aqueous alcohol in the rhombic system,  $a:b:c=0.6868:1.08548$  (Oebbecke, Ber. 1884, **17**, 1725); m.p. 208° (213° corr.) decomp. (Fischer, *ibid.* 1889, **32**, 2451); 224–225° (corr.) decomp. (Abderhalden, Z. physiol. Chem. 1910, **64**, 540); 211° when heated rapidly (Skola, Z. Zuckerind. Czechoslov. 1920, **44**, 347); decomposes at 247–249° (Dunn and Brophy, J. Biol. Chem. 1932, **99**, 221). The crystals exhibit piezo-electric phenomena. It is sparingly soluble in water (0.88 g. in 100 g. at 25°) but the solubility is raised in the presence of alkali and alkaline earth salts (Pfeiffer, Ber. 1915, **48**, 1938); it is insoluble in methyl or ethyl alcohol (less than 0.007 g. in 100 g. at 25°), ether and acetone and practically insoluble in cold glacial acetic acid (Pertzoff, J. Biol. Chem. 1933, **100**, 97). For the solubility in water-alcohol mixtures at various temperatures, *see* Dunn and Ross (*ibid.* 1938, **125**, 309). The heat of combustion is 966 kg.-cal. and the heat of solution in water is 9,600 g.-cal. (Pertzoff, *l.c.*). For the free energy,  $\Delta F_{298}^{\circ}$  (crystalline) = –170,700 g.-cal. and the values of  $\Delta H$  and  $\Delta S$ , *see* Borsook and Huffmann, *ibid.* 1933, **99**, 663; J. Amer. Chem. Soc. 1932, **54**, 4297; Huffmann, Ellis and Fox, *ibid.* 1936, **58**, 1728. The dissociation constants of glutamic acid are  $K_a' 5.62 \times 10^{-6}$  and  $2.19 \times 10^{-10}$ ,  $K_a' 1.55 \times 10^{-12}$  (Kirk and Schmidt, J. Biol. Chem. 1929, **81**, 237; Harris, *ibid.* 1929, **84**, 179); *see* Schmidt, Kirk and Appleman (*ibid.* 1930, **88**, 285) for the values at 0°, and also Neuberger (Biochem. J. 1930, **30**, 2085); Wilson and Cannan (J. Biol. Chem. 1937, **119**, 309). In aqueous solution  $[\alpha]_D^{20} + 12.04^\circ$ , and  $[\alpha]_D^{25} + 11.0^\circ$ ; in 10% aqueous hydrochloric acid  $[\alpha]_D^{20} + 34.9^\circ$ . Increasing amounts of strong acid cause a continuous increase in the specific rotation, which tends towards a maximum. The addition of bases first changes the dextro- into laevo-rotation, which attains its highest numerical value with the formation of the acid salt, further quantities of base convert the laevo-rotation again to a dextro-rotation. With lead hydroxide, no change in sign of the rotation takes place (Andrlík, Z. Ver. Rubenzuck.-Ind. Böhm. 1903, 948; *see also* Pellet, Chem. Zentr. 1911, I, 1766). When an aqueous solution of *d*-glutamic acid is boiled, an equilibrium is set up between the *d*-glutamic acid and its dehydration product *l*-pyrrolidone-2-carboxylic acid, the position of equilibrium depending on the  $p_H$ . In solutions near neutrality, dehydration is favoured but slow at 100°; in solutions greater

than 2*M* with respect to hydrochloric acid or 0.5*M* to sodium hydroxide reversion to glutamic acid occurs (Skola, Z. Zuckerind. Czechoslov. 1920, **44**, 347; Foreman, Biochem. J. 1914, **8**, 492; Fischer and Bochner, Ber. 1911, **44**, 1332; and for the equilibrium constants at various  $p_H$  values, *see* Wilson and Cannan, *l.c.*). The optical properties of the equilibrium solutions at various  $p_H$  values indicate that the first stage in the dehydration is the formation of an internal salt (Okinaka, A. 1928, 435). Staněk (Z. Zuckerind. Böhm. 1912, **37**, 1) on heating the aqueous solution above 200°, obtained *dl*-pyrrolidone-carboxylic acid, below that temperature the laevo-rotatory form is the chief product.

A solution of *d*-glutamic acid (1:22,000) gives a characteristic colour reaction with triketohydrindene (Abderhalden and Schmidt, Z. physiol. Chem. 1913, **85**, 143).

When glutamic acid is administered as a food, 96% is absorbed, a portion being used in protein synthesis and the rest oxidised to urea (Andrlík and Velich, Z. Zuckerind. Böhm. 1908, **32**, 313; Butts, Blunden and Dunn, J. Biol. Chem. 1937, **119**, 247). Its administration to phloridizimmed dogs leads to increased elimination of *d*-glucose in the urine (Warkalla, Beitr. Phys. 1914, **1**, 91) and in normal animals increases the excretion of urea and sulphate (Stekol and Schmidt, Univ. California Pub. Physiol. 1933, **8**, 31; A. 1934, 440). Glutamic acid shows little toxicity (Sullivan, Hess and Sebrrell, U.S. Publ. Health Repts. 1932, **47**, 75) and is used in foods in the form of the sodium salt which has a strong meat-like flavour (*see* B.P. 269576). *In vitro* it is hæmotoxic to the blood corpuscles of warm-blooded animals (Sulmann, Z. Immunitätsforsch. 1932, **74**, 45), but its copper, iron, manganese and magnesium salts are effective in preventing anæmia in rats (Brand and Stucky, Proc. Soc. Exp. Biol. Med. 1934, **31**, 627, 689, 739). For its effect on hæmoglobin production, *see also* Drabkin and Miller (J. Biol. Chem. 1931, **90**, 531); and for its hyperglycæmic action, *see* Nord (Acta med. scand. 1926, **65**, 1, 61).

For its katabolism in the animal organism, *see* Ringer *et al.* (J. Biol. Chem. 1913, **14**, 541) and also the series of papers dealing with the intermolecular transfer of amino-groups between glutamic and pyruvic acids by Braunstein and Kritzmann (Biochimia, 1937, **2**, 242, 859; Enzymologia, 1937, **2**, Pt. III, 129; Nature, 1937, **40**, 503) and by Von Euler, Adler, Das *et al.* (Z. physiol. Chem. 1938, **254**, 61; Arkiv Kemi, Min., Geol. 1938, **12B**, No. 40). For the biological dehydrogenation, *see idem.*, Compt. rend. Trav. Lab. Carlsberg, 1938, **22**, 15; 1938, A III, 438; and for the oxidation of its phenyl derivatives in the animal body, *see* Von Beznák, Biochem. J. 1929, **205**, 420; Oesterlin, *ibid.* 1929, **215**, 203.

Fermentation of glutamic acid by members of the genus *Clostridium* which are widely distributed in soil, gives rise to *n*-butyric and acetic acids, carbon dioxide, ammonia and hydrogen (Barker, J. Bact. 1938, **36**, 322). Under the influence of strictly anaerobic spore-forming bacteria from soil the fermentation leads to the formation of acetic and propionic acids (*idem.*, Enzymologia, 1937, **2**, 175, *cf.* Brasch and

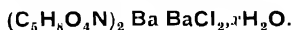
Neuberg, *Biochem. Z.* 1908, **13**, 299). Alcoholic fermentation gives methyl alcohol (Leoncini, *Boll. ist. super. agrar. Pisa*, 1934, **10**, 418). Decarboxylation by certain (legume) bacteria yields  $\gamma$ -aminobutyric acid and carbon dioxide (Virtanen, Rintala and Laine, *Nature*, 1938, **142**, 674; Ackermann, *Z. physiol. Chem.* 1910, **69**, 273; Abderhalden, *ibid.* 1913, **85**, 131). Certain bacilli cause the formation of a polypeptide from glutamic acid (Ivanovics, *Zentr. Bakt.* 1938, **1**, 142, 52). For the conversion to glutamine by enzymes, *see* Krebs (*Biochem. J.* 1935, **29**, 1951). Glutamic acid breaks down under the action of sunlight to propaldehyde, ammonia and carbon dioxide, especially in the presence of sensitizers such as aluminium, titanium and zinc oxides (Ganassini, *Giorn. Farm. Chim.* 1912, **81**, 226; Rao and Dhar, *J. Indian Chem. Soc.* 1934, **11**, 617). Dissociation of the carboxyl groups occurs on absorption of ultra-violet light (Anslow, *Phys. Rev.* 1932, **40**, 115). Oxidation of glutamic acid with hot sodium dichromate or potassium permanganate in sulphuric acid, or with hydrogen peroxide, yields succinic acid (Dakin, *J. Biol. Chem.* 1909, **5**, 409; Chu and Tseng, *J. Chinese Chem. Soc.* 1933, **1**, 46). The action of sodium hypobromite in alkaline solutions gives glutarimonoaldehyde; in neutral solution the product is  $\beta$ -cyanopropionic acid (Friedman and Morgulis, *J. Amer. Chem. Soc.* 1936, **58**, 909). Electrolytic oxidation in dilute sulphuric acid yields succinic and succinamic acids, succinimide and further breakdown products (Takayama, *J. Chem. Soc. Japan*, 1931, **52**, 155; *Bull. Chem. Soc. Japan*, 1933, **8**, 125). The direct oxidation of glutamic acid with oxygen is catalysed by adrenaline, pyrocatechol and related compounds with the intermediate formation of glyoxylic acid and finally ammonia, formaldehyde and carbon dioxide (Barrenschecan and Danzer, *Z. physiol. Chem.* 1933, **220**, 57). In the presence of charcoal this oxidation leads to the formation of urea (Arni, *Biochem. Z.* 1930, **226**, 233). For the oxidation with silver oxide, *see* Herbst and Clarke (*J. Biol. Chem.* 1934, **104**, 769).

When treated with nitrous acid glutamic acid yields  $\alpha$ -hydroxyglutaric acid (glutamic acid, *q.v.*) (Ritthausen, *J. pr. Chem.* 1868, [1], 103, 239). Natural *d*-glutamic acid is converted by nitrous acid into *l*- $\alpha$ -hydroxyglutaric acid, and by nitrosyl chloride or hydrochloric acid and nitrous acid into *l*- $\alpha$ -chloroglutamic acid, which in turn yields *d*- $\alpha$ -hydroxyglutaric acid (Fischer and Moreschi, *Ber.* 1912, **45**, 2447).

For electrolytic diazotisation of the acid, *see* Krauss (*J. Amer. Chem. Soc.* 1917, **39**, 1427).

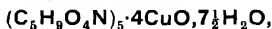
*d*-Glutamic acid forms normal and acid salts, the latter being the more common. Of these the sodium,  $C_5H_8O_4NNa$ ; potassium,  $C_5H_8O_4NK$ ; calcium,  $(C_5H_8O_4N)_2Ca$ ; barium,  $(C_5H_8O_4N)_2Ba$ ; lead,  $(C_5H_8O_4N)_2Pb$  salts, prepared by neutralisation or double decomposition in aqueous solution, are crystalline and hygroscopic. The glutamates of general formula  $C_5H_8O_4NM^{1/2}$  are readily soluble in water and have a characteristic meat-like flavour. The manufacture and consumption of the sodium salt are general in China and Japan (Ikeda, *Orig. Com. 8th Intern. Cong. Appl. Chem.* 1912, **18**,

147; Tseng and Chu, *Acad. Sin. Mem. Nat. Res. Inst. Chem.* 1931, No. 5, 1; Han, *Ind. Eng. Chem.* 1929, **21**, 984). The disodium salt can be prepared by adding the acid dissolved in liquid ammonia to sodium in liquid ammonia until the blue colour disappears (Voss and Guttman, *Ber.* 1930, **63** [B], 1726). For its Raman spectrum, *see* *J. Chem. Phys.* 1937, **5**, 508. The acid sodium salt is converted to sodium pyrrolidonecarboxylate on heating to 150–160° (Tseng and Chu, *Sci. Quart. Peking*, 1932, **3**, 1) and the calcium salt cyclises at 180–185° (Abderhalden, *Z. physiol. Chem.* 1910, **64**, 447); it is precipitated quantitatively from aqueous solution if sufficiently concentrated (Foreman, *Biochem. J.* 1914, **8**, 479). For solubility data of the dibasic calcium salt, *see* Takayama (*J. Soc. Chem. Ind. Japan*, 1930, **33**, Suppl. binding, 91). The normal barium salt is almost insoluble in water (Siegfried and Schutt, *Z. physiol. Chem.* 1912, **81**, 261). If the hydrochloride, hydrobromide or hydriodide of glutamic acid be boiled in aqueous solution with freshly precipitated calcium or barium carbonate, the filtrate on concentration deposit well formed crystals of a salt of the type



The corresponding strontium compounds are obtained by crystallising the glutamate with excess halide (Anslow and King, *Biochem. J.* 1927, **21**, 1168). For the transference numbers and conductivities of the sodium, calcium and barium salts, *see* Miyamoto and Schmidt (*J. Biol. Chem.* 1933, **99**, 335; *also* *Univ. Calif. Pub. Physiol.* 1932, **8**, 9). The normal ammonium salt,  $(NH_4)_2C_5H_7O_4N$ , loses  $NH_3$  at 110–115°, and forms the acid salt  $(NH_4)C_5H_7O_4N$ ;  $[\alpha]_D$  about  $-3.6^\circ$  (Schulze and Trier, *Ber.* 1912, **45**, 257). Evaporation of *d*-glutamic acid with aqueous ammonia causes decomposition of the ammonium salt but with ammonium chloride the acid salt is formed (Tseng and Chu, *Sci. Rep. Nat. Univ. Peking*, 1936, **1**, No. 4, 17), which is also obtained by dissolving the acid in liquid ammonia (Voss and Guttman, *l.c.*).

The blue copper derivative,



is crystalline; zinc and cadmium salts and cobalt and nickel derivatives have been prepared (Hugounenq and Florence, *Bull. Soc. chim.* 1920, [iv], 27, 750). Wolff described an amorphous greenish-blue copper salt as



which dissolves in 400 parts of boiling water (*Annalen*, 1890, **260**, 79); Pfeiffer and Werner formulate the copper salt



since it reacts with sodium hydroxide precipitating copper hydroxide and forming a bluish-violet solution which contains a substance precipitated by alcohol and having the required Cu:N ratio (*Z. physiol. Chem.* 1937, **246**, 212). For an asymmetric synthesis of optically active cobalt complexes with the formula  $[Co(C_5H_7O_4N)_3]Na_3$ , *see* Lifschitz *Proc. Acad. Sci. Amsterdam*, 1936, **39**, 1192). Two

forms of this complex, each having *d*- and *l*-forms, have been described; one is red with insoluble silver and lead salts, the other violet with salts soluble in boiling water. The *silver salts*,  $C_5H_7O_4Na_2$  and  $C_5H_7O_4Na$ , are white insoluble powders; the *ferrous salt* is obtained when glutamic acid is boiled with an excess of iron powder in an oxygen-free atmosphere (Hoffmann, G.P. 264390); the *zinc salt* is basic ( $C_5H_7O_4N_2$ ),  $Zn \cdot ZnO$ ; the *mercuric salt* a heavy crystalline powder decomposing at 208–209° (Habermann, Annalen, 1871, 179, 248; Abderhalden and Kautzsch, Z. physiol. Chem. 1910, 64, 447; 68, 487; 1912, 78, 333). The *hydrochloride* has m.p. 202°, or heated rapidly, m.p. 213° (Abderhalden, Z. physiol. Chem. 1910, 64, 450); when precipitated from hydrochloric acid solution it contains 2 mol.  $H_2O$  (Wei and King, Science, China, 1936, 19, 354). It has  $[\alpha]_D^{20} +25^\circ$  (Abderhalden, *l.c.*); or 24.5° (Fischer and Boelmer, Ber. 1911, 44, 1334). For crystallography of the hydrochloride, see Kaplanova (Abh. Bohm. Akad. 1915, No. 23, from Jahrb. Min. 1917, 1, 123), and for the Raman spectrum, see Edsall (J. Chem. Physics, 1937, 5, 508). Data are given by Takayama for its identification with the polarising microscope (J. Chem. Soc. Japan, 1931, 52, 245). *d*-Glutamic acid *picrolonate* has  $[\alpha]_D^{20} +85^\circ$  (Levene and Van Slyke, J. Biol. Chem. 1912, 12, 127). The *strychnine salt* has m.p. 225–230°,  $[\alpha]_D^{20} -25.5^\circ$ ; the *brucine salt* has m.p. 240°,  $[\alpha]_D^{20} -23^\circ$  (Dakin, Biochem. J. 1919, 13, 398). For the *imido-orthophosphoric ester*,  $C_7H_{14}O_7NP$ , of glutamic acid, see Langheld (Ber. 1911, 44, 2076). The  *$\alpha$ -ethyl ester* has m.p. 110° (Neuberger, Biochem. J. 1936, 30, 2085); the  *$\gamma$ -ethyl ester* forms prisms from 50% alcohol, m.p. 194° (188° Menozzi and Appiani, Gazzetta, 1894, i, 24, 384), *hydrochloride* m.p. 134°. The *diethyl ester* is an oil with b.p. 139–140°/10 mm.,  $d^{17} 1.0737$  and  $[\alpha]_D^{20} +7.34^\circ$  (Fischer, Sitzungsber. Akad. Wiss. Berlin, 1900, 48, 1062), and is very soluble in water. For the dissociation constants of the ethyl esters, see Neuberger (*l.c.*).

Glutamic acid forms a soluble *benzene sulphonyl derivative*,



m.p. 129–132°, which can easily be methylated to *N*-benzenesulphonylmethylglutamic acid, m.p. 138–139°, or esterified to the di-*n*-butyl ester, m.p. 58–59° (Hedin, Ber. 1890, 23, 3196; Gurin J. Amer. Chem. Soc. 1936, 58, 2140; see also Z. physiol. Chem. 1937, 250, 189). The *p*-toluene sulphonyl derivative is an oil but gives a di-*n*-butyl ester, m.p. 64–65°, and a methylated derivative, m.p. 131–132° (McChesney and Swann, jun. J. Amer. Chem. Soc. 1937, 59, 1116). *Glutamic-N-sulphonic acid* is obtained by the action of *N*-pyridinium sulphonic acid; its potassium salt crystallises with acetic acid:  $2C_5H_7O_4NSK_3 \cdot C_2H_3CO_2H$  and forms double salts with acid potassium glutamate,



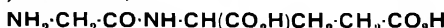
(Baumgarten, Marggraff and Dammann, Z.

physiol. Chem. 1932, 209, 145). *Acetyl-d-glutamic acid*, m.p. 199°, is formed when ketene is passed into an aqueous solution of *d*-glutamic acid (Bergmann and Stern, Ber. 1930, 63 [B], 37); or from the sodium salt and acetic anhydride (Nicolet, J. Amer. Chem. Soc. 1930, 52, 192), but the sodium salt of acetylglutamic acid is readily racemised in aqueous solution by acetic anhydride (Du Vigneaud and Meyer, J. Biol. Chem. 1932, 98, 295). The acetyl derivative readily gives, with methyl sulphate, *acetylmethylglutamic acid*, decomp. 203° (Knoop and Oesterlin, Z. physiol. Chem. 1927, 170, 186).

*Chloracetyl-d-glutamic acid*,



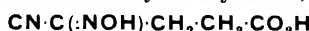
n.p. 143° (corr.),  $[\alpha]_D^{20} -13.5^\circ$  ( $\pm 0.2^\circ$ ) in aqueous solution; with ammonia it yields *glycyl-d-glutamic acid*,



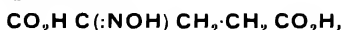
Fischer, Ber. 1907, 40, 3704; Fischer, Kropp and Stahlschmidt, Annalen, 1909, 365, 181). *Phenylacetylglutamic acid*,  $C_{13}H_{15}O_5N$ , microscopic needles, has m.p. 132°,  $[\alpha]_D^{20} -19^\circ$  in 3–10% aqueous solution; the *brucine salt* has  $[\alpha]_D^{20} -1.37^\circ$  (Thierfelder, Sherwin, Z. physiol. Chem. 1915, 94, 1; Ber. 1915, 47, 2630). *o*-Nitrobenzoylglutamic acid, m.p. 151°, is formed from the hydrochloride and *o*-nitrobenzoyl chloride in the presence of magnesium oxide. The formation of *N*-carboxylglutamic acid in sugar solutions containing glutamic acid and carbon dioxide is suggested by Majer (Listy Cukrovar, 1928, 47, 123; Amer. Chem. Abstr. 1929, 23, 728). For the *half amide* of glutamic acid, m.p. 209° (decomp.), see Voss and Guttman (Z. physiol. Chem. 1932, 204, 1); for the synthesis of *N*-alkyl derivatives, see Sugawara (J. Pharm. Soc. Japan, 1927, No. 550, 1041); and for  *$\gamma$ -phenylglutamic acid*, see von Beznák (Biochem. Z. 1929, 205, 414). Numerous di- and poly-peptides have been synthesised from glutamic acid and the original literature should be consulted for descriptions of these substances.

*dl*-Glutamic Acid is obtained in 60–65% yield from the *d*-acid or its acid sodium salt by heating with solid ammonium chloride at 230–235° for an hour and then refluxing for 5 hours with 6*N*-hydrochloric acid. Anhydrous *dl*-glutamic acid and the monohydrate were obtained in this way by Dunn and Stoddard (J. Biol. Chem. 1937, 121, 521). A slightly better yield (71%) is obtained by heating the *d*-acid with barium hydroxide in aqueous solution for 9 hours at 160–170°. Sodium carbonate, bicarbonate and hydroxide and calcium hydroxide do not cause racemisation (Tseng and Chu, J. Chinese Chem. Soc. 1933, 1, 188; Schulze and Bosshard, Ber. 1885, 18, 388; Schulze, Z. physiol. Chem. 1892, 9, 253). Syntheses of *dl*-glutamic acid have been carried out by Wolff (Annalen, 1890, 260, 79), by Knoop and Oesterlin (Z. physiol. Chem. 1927, 170, 186), and by Dunn, Smart, Redemann and Brown (J. Biol. Chem. 1931, 94, 599). Wolff started with lævulinic acid and by boiling dibromolævulinic acid with water, obtained glyoxylpropionic acid,  $OHC \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , which reacts with hydroxylamine to form  $\gamma$ -*diisontrovaleric*

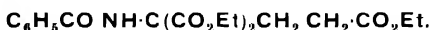
acid,  $\text{CH}(\text{:NOH})\text{C}(\text{:NOH})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , from which isonitrosocyanobutyric acid,



is obtained by dehydration with sulphuric acid and subsequent treatment with cold sodium hydroxide. When isonitrosocyanobutyric acid is hydrolysed with boiling alkali, it yields isonitrosoglutaric acid,



and this is reduced to inactive glutamic acid by tin and hydrochloric acid. Knoop and Oesterlin's method consisted in the reduction of  $\alpha$ -ketoglutaric acid in the presence of ammonia; cf. Shemin and Herbst, J. Amer. Chem. Soc. 1938, **60**, 1954. The third synthesis started from the isonitroso-derivative of malonic ester, ethyl oximmonmalonate,  $\text{HON}\cdot\text{C}(\text{CO}_2\text{Et})_2$ . On reduction with aluminium amalgam, this gives ethyl aminomalonate which was benzoylated and then condensed with  $\beta$ -bromopropionic acid to ethyl  $\alpha$ -benzamidopropionic- $\alpha\gamma$ -tricarboxylate,



This ester, on hydrolysis, gives *dl*-glutamic acid which forms rhombic plates from water, m.p. 199° (Dunn, Smart *et al.*, *l.c.*, show photomicrographs of *d*- and *dl*-glutamic acids); Dunn and Brophy give the m.p. as 225–227° (J. Biol. Chem. 1932, **99**, 221). It is soluble in hot water and sparingly soluble in cold water (1 part in 66.7 parts at 20°), also sparingly in alcohol, ether, light petroleum and carbon disulphide. The flavours of the sodium, potassium, lithium, calcium, barium, strontium, magnesium, methyl ammonium (m.p. 75°; hydrochloride, m.p. 168–169°), and dimethylammonium (hydrochloride, m.p. 178.5°) salts have been described (Tseng and Chu, *l.c.*). The potassium and methylammonium salts are hygroscopic. The copper salt,  $\text{C}_5\text{H}_7\text{O}_2\text{NCu}_2\cdot 2\frac{1}{2}\text{H}_2\text{O}$ , forms blue needles, becomes anhydrous at 135° and is not soluble in less than 1,000 parts of boiling water. A number of derivatives have been reported: the hydrochloride crystallises in needles, m.p. 193° (Wolff), 200° (Abderhalden and Kautsch, Z. physiol. Chem. 1910, **68**, 487), and is crystallographically identical with the hydrochloride of the *d*-acid,  $a:b:c=0.8873:1.0:3.865$  (Wolff, *l.c.*); the acid sulphate, m.p. 164.6°; picrolonate, fine short spindles, decomposing at 184° (Levene and van Slyke, J. Biol. Chem. 1912, **12**, 127); the *N*-chloroacetyl derivative has m.p. 123°, formyl, m.p. 181.7°; acetyl, m.p. 187.5°; propionyl, m.p. 173.1°; *n*-butyryl, m.p. 179°; and isovaleryl, m.p. 180.6°. The hydrochloride of the ethyl ester has m.p. 113.1° (Tseng and Chu, *l.c.*). *dl*-Benzoyl-glutamic acid crystallises with  $\text{H}_2\text{O}$ , m.p. 152–153° (155–157° corr.), and is soluble in 124 parts of water at 20° (Fischer, Ber. 1899, **32**, 2451).

When *dl*-glutamic acid is crystallised from water, right- and left-handed enantiomorphous crystals are deposited, but the fact cannot conveniently be utilised for resolution and the preparation of the *l*-isomeride; this was, however, effected by the cultivation of *Penicillium glaucum* in a solution of the *dl*-acid, whereby the *d*-acid

is destroyed and the *l*-acid remains in solution (Menozzi and Appiani, Gazzetta, 1894, **1**, 24, 370). Fischer (Ber. 1899, **32**, 2451) resolved *dl*-glutamic acid by the fractional crystallisation of the strychnine salt. The optical resolution is best carried out by converting *dl*-glutamic acid to *dl*-pyrrolidonecarboxylic acid by heating to the melting-point and resolving the latter acid by heating with an equimolecular portion of quinine in the presence of water. The quinine salts are easily separated by successive treatment with alkali, acid and absolute alcohol. The mother liquor, after separation of the *d*-acid, is concentrated *in vacuo*, filtered, hydrolysed with normal sodium hydroxide, neutralised and dried *in vacuo*. Extraction with alcohol and evaporation give the *l*-pyrrolidonecarboxylic acid. Recovery of *d*-glutamic acid from the *l*-pyrrolidonecarboxylic acid and *l*-glutamic acid from the *d*-pyrrolidonecarboxylic acid is readily effected by heating with 15% hydrochloric acid (Sugasawa, J. Pharm. Soc. Japan, 1926, No. 537, 934).

*l*-Glutamic Acid is usually obtained by resolution of *dl*-glutamic acid (*v. supra*) but it may be obtained by the cultivation of certain bacilli, e.g. *B. mesentericus*, on *d*-glutamic acid thereby forming a polypeptide-like substance the difficultly soluble copper salt of which is hydrolysed by hydrochloric acid to *l*-glutamic acid (Bruckner and Ivánovics, Z. physiol. Chem. 1937, **247**, 281). A theoretical yield of *l*-glutamic acid is given on hydrolysis with hydrochloric acid of the purified capsular substance of anthrax bacillus (*idem*, Z. Immunitätsforsch. 1938, **93**, 119).

*l*-Glutamic acid forms leaflets from water, m.p. 213°, with decomposition (rapid heating). It is tasteless and has  $[\alpha]_D^{20} -12.9^\circ$  in water. The crystal structure has been studied by Bernal (Z. Krist. 1931, **78**, 363, in English). *l*-Glutamic acid hydrochloride has m.p. 200–204° and  $[\alpha]_D^{20} -30.06^\circ$ . Data are given by Takayama (J. Chem. Soc. Japan, 1931, **52**, 245) for its micro-identification with the polarising microscope. Benzoyl-*l*-glutamic acid has m.p. 130–132°, dissolves in less than 2 parts of water at 100°, or 21 parts at 20°, and has  $[\alpha]_D +13.81^\circ$  in 5% aqueous solution, and the potassium salt has  $[\alpha]_D -18.7^\circ$ ; it yields *l*-glutamic acid on hydrolysis and by the Curtius degradation gives *l*-benzamido-1:3-diaminopropane hydrochloride, m.p. 158° (picrate, m.p. 100°), which is hydrolysed to  $\beta$ -aminopropaldehyde (*dimedone* derivative, m.p. 208–209°) (Bergmann, Zervas and Schneider, J. Biol. Chem. 1936, **113**, 341).

#### $\beta$ -Hydroxyglutamic Acid,



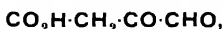
The isolation of  $\beta$ -hydroxyglutamic acid from the product of hydrolysis of caseinogen with 25% sulphuric acid has been described by Dakin (Biochem. J. 1918, **12**, 290) and by Gulland and Morris (J.C.S. 1934, 1644). According to the later authors, the hydrolysate is neutralised to Congo Red with barium hydroxide and the barium sulphate, which adsorbs all the  $\beta$ -hydroxyglutamic acid, is eluted with 1% hydrochloric acid at 25°. The amino-acids so obtained are treated to remove glutamic and

aspartic acids, *l*-leucine and other amino-acids, and the barium salt of  $\beta$ -hydroxyglutamic acid is separated. This salt on crystallisation decomposes to give the monohydrate,



similar to Dakin's specimen. Syntheses of  $\beta$ -hydroxyglutamic acid have been described by Dakin (from glutamic acid, *Biochem. J.* 1918, **12**, 290; 1919, **13**, 398) and by Harington and Randall (by catalytic hydrogenation of the  $\alpha$ -isonitroso derivative of ethyl acetonedicarboxylate, *ibid.* 1931, **25**, 1917), but there were marked discrepancies between the products from these two syntheses.

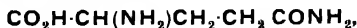
The estimation of  $\beta$ -hydroxyglutamic acid is best made after a preliminary purification by electrodialysis. The anode liquid is then freed from methionine with *n*-butyl alcohol and oxidised with chloramine-T. The product,



is not isolated but determined as the *p*-nitrophenylosazone (Gulland and Morris, *l.c.*). The anhydrous *dl*-acid has m.p. 195° with decomposition and is soluble in water but insoluble in alcohol. The hydrochlorides of the *dl*-acid and of its ethyl ester have m.p. 87° and 168.5° respectively. The *silver*, *copper* and *acid calcium* salts have been prepared (Harington and Randall, *l.c.*). *d*- $\beta$ -Hydroxyglutamic acid crystallises from water in prisms which sinter at 100°; it is soluble in water and acetic acid, sparingly soluble in methanol and insoluble in ethyl alcohol and ether. Its isoelectric point occurs at  $p_{\text{H}}$  3.28. For the dissociation constants, see Kirk and Schmidt, *J. Biol. Chem.* 1929, **81**, 237. In aqueous solution (4%) it has  $[\alpha]_{\text{D}}^{20}$  about +0.8° and in 2% hydrochloric acid solution  $[\alpha]_{\text{D}}^{20} + 16.3^\circ$ . On prolonged heating at 100–110° over phosphorus pentoxide it yields hydroxypyrrolidonecarboxylic acid. It yields *silver*, *copper*, *mercury*, *lead*, *cadmium*, *zinc*, *calcium* and *barium* salts of which the silver and mercury salts only are insoluble, and it gives a *diethyl ester*, m.p. 62–63°, which is converted, in the presence of light and moisture, into ethyl hydroxypyrrolidonecarboxylate, m.p. 115°, and on boiling with concentrated hydrochloric acid to  $\alpha$ -ketoglutaric acid (Abderhalden and Murke, *Z. physiol. Chem.* 1937, **247**, 227). The *benzoyl* derivative has m.p. 175–176° and the derived hydantoin, 191–193° (Knoop *et al.*, *ibid.* 1936, **239**, 30). The *brucine* salt has m.p. 200°, with decomposition and  $[\alpha]_{\text{D}}^{20} - 25.0^\circ$ . The *strychnine* salt has m.p. 245° and  $[\alpha]_{\text{D}}^{20} - 26.3^\circ$ . When heated with hydriodic acid at 150°, *d*- $\beta$ -hydroxyglutamic acid is converted to *d*-glutamic acid. As a hydroxy-acid, it gives colour reactions with phenols and concentrated sulphuric acid, purple with resorcinol, bright green with thymol and red (flesh) with phloroglucinol.

M. A. W.

## GLUTAMINE,



is a half amide of glutamic acid. It was discovered in 1877 by Schulze and Urlich (Ber.

1877, **10**, 85) in the juice of young pumpkin plants and isolated from beet-root sap by Schulze and Bosshard (*ibid.* 1883, **16**, 312), 1 litre yielding 0.7–0.9 g. of glutamine; see also Smolenski (*Chem. Zentr.* 1911, **I**, 518, from *Z. Ver. deut. Zucker-Ind.* 1910, 1215), Schulze (*Z. physiol. Chem.* 1894, **20**, 327; 1897, **24**, 18; Ber. 1896, **29**, 1882; Landw. Versuchs.-Stat. 1898, **49**, 442) and Deleano (*Z. physiol. Chem.* 1912, **80**, 79). It appears to replace its homologue, asparagine, in some families, e.g. *Caryophyllaceæ*, *Cruciferae* and *Filices*, where it occurs in the leaves, seedlings, roots and tubers. The amount of glutamine found in seedlings, etc., is only about 3% of the dry weight, which is much less than the amount of asparagine found in leguminous seedlings. The glutamine content does not appear to be constant but, for example, in the beetroot, it increases in the growing plant, reaches a maximum and then disappears, apparently being replaced by allantoin (Ravenna and Nucorini, *Annali Chim. Appl.* 1928, **18**, 509). By the application of ammonium sulphate, the glutamine content can be raised to 5.4% of the dry weight (Vickery, Pucher and Clark, *Plant Physiol.* 1936, **11**, 413). It appears to be a direct product of the hydrolysis of proteins during germination (Nucorini, *Annali Chim. Appl.* 1930, **20**, 239). Glutamine is widely distributed in plants; thus, it occurs with asparagine in the juice of ripening oranges (Scurti and de Plato, *Chem. Zentr.* 1908, **11**, 1370); in rhubarb leaves (Vickery, Pucher, Leavenworth and Wakeman, *J. Biol. Chem.* 1938, **125**, 527) and in appreciable amounts in tobacco leaves, accounting for the formation of ammonia when the leaves are boiled with water (Vickery and Pucher, *J. Biol. Chem.* 1936, **113**, 157). The white exudation which appears on the tip of Chewing's fescue grass, after the application of ammonium sulphate, has been identified as glutamine (Doak, New Zealand *J. Sci. Tech.* 1937, **18**, 844). For distribution and rôle in plants, see also Stieger (*Z. physiol. Chem.* 1913, **86**, 245) and Schwab (*Planta*, 1935, **24**, 160; 1936, **25**, 579). According to Thierfelder and von Cramm, glutamine is a component of protein molecules (*Z. physiol. Chem.* 1919, **105**, 58). For the formation of glutamine by enzymic digestion of gliadin, see Damodaran, Jaaback and Chibnall, *Biochem. J.* 1932, **26**, 1704.

The isolation of glutamine from beetroot can be effected by the method of Schulze and Bosshard (*l.c.*), modified in detail by Vickery, Pucher and Clark (*J. Biol. Chem.* 1935, **109**, 39). The roots are ground and pressed out. The residue is cytolyzed in ether for 30 minutes and on pressing again the glutamine is expressed. The juice is treated with lead acetate, filtered and precipitated with mercuric nitrate at neutrality. The precipitate is decomposed with 10% sulphuric acid and with hydrogen sulphide and the filtrate is concentrated *in vacuo* at not more than 60°C., refiltered and concentrated to crystallisation, when 2 vol. of ethyl alcohol are added. The product is crystallised from water by adding 2 vol. of alcohol. A similar method of extracting glutamine from expressed beet juice (giving 3.4 g. per litre) has been described by Eisenchimmel (*Z. Zuckerind. Czechoslov.* 1927, **51**, 337). The

synthesis of *d*-glutamine from *d*-glutamic acid has been carried out by Nienburg (Ber. 1935, **68** [B], 2232). The  $\gamma$ -ethyl ester of glutamic acid was converted to the carbobenzyloxy derivative and treated with liquid ammonia at 15–20° and the amide so formed,



was hydrogenated in the presence of palladium catalyst to *d*-glutamine. The  $\gamma$ -esters of glutamic acid have also been converted to the amide (glutamine) by way of the hydrazide and azide (B.P. 437873). For the conversion of *d*-glutamic anhydride to *d*-glutamine, see Bergmann, Zervas and Salzmann, Ber. 1933, **66** [B], 1288. For the biochemical synthesis of glutamine from ammonium glutamate, see Krebs, Biochem. J. 1935, **29**, 1951.

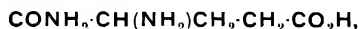
Glutamine crystallises in needles from aqueous alcohol, m.p. 184–185°; it dissolves in about 25–7 parts of water at 16° (Schulze and Godet, Landw. Versuchs-Stat. 1907, **67**, 313) and is sparingly soluble in alcohol. It is unstable in aqueous solution (Damodaran, Jaaback and Chibnall, *l.c.*) and behaves as a very weak acid towards indicators (Sellier, Chem. Zentr. 1904, **1**, 789). Glutamine is dextrorotatory in aqueous solution; seven specimens from various vegetable sources were found to have  $[\alpha]_D^{20}$  between +1.9° and +9.5°, the differences being probably due to the presence of the two stereoisomers in varying proportions (Schulze and Bosshard, Ber. 1885, **18**, 390; Sellier, *l.c.*; Schulze, Ber. 1906, **39**, 2932; Landw. Versuchs-Stat. 1906, **65**, 237). Schulze and Trier (Ber. 1912, **45**, 257) found that a 4% aqueous solution of glutamine, purified through its copper salt, has  $[\alpha]_D^{20}$  +6° to +7°, while for synthetic samples, Bergmann, Zervas and Salzmann (*l.c.*) give  $[\alpha]_D^{20}$  +8.0° and Nienburg (*l.c.*)  $[\alpha]_D^{20}$  +8.3°. A 7–8% solution in 5% hydrochloric acid has  $[\alpha]_D^{20}$  +31° to +32° (Schulze and Trier, *l.c.*, cf. Pellet, Chem. Zentr. 1911, **1**, 1766, from Z. Zuckermnd. Bohm. 1911, **35**, 437). For the refractive index, density and  $[\alpha]$  of solutions of glutamine, see Eisen-schmelmel (*l.c.*). The isoelectric point is 8.0 to 10.0 (Errera, Compt. rend. 1931, **193**, 1347). In the presence of liver tissue, glutamine is converted into urea (Leuthardt, Z. physiol. Chem. 1938, **252**, 238); for the action of asparaginase on glutamine and also on asparagine, see Geddes and Hunter, J. Biol. Chem. 1928, **77**, 197.

The estimation of glutamine can be effected by Schlosing's method (Schulze, J. pr. Chem. 1885, [u], **31**, 233), ammonium salts being removed by distillation with magnesium at a pressure sufficiently reduced to cause the solution to boil at 40°. Under these conditions the amide group is not hydrolysed (Sellier, Bull. Soc. chim. Sucr. Dist. 1907, **25**, 124; Schulze, Landw. Versuchs-Stat. 1906, **65**, 237). More recent determinations of glutamine by hydrolysis were carried out in solutions buffered to  $p_H$  6.5 (Chibnall *et al.*, Biochem. J. 1935, **29**, 2710; Mendel and Vickery, Carnegie Inst. Washington Yearbook, 1935, **34**, 298). The van Slyke determination of amino-compounds using nitrous acid gives abnormal results with glutamine but normal with asparagine, and these differences

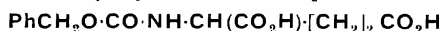
have been applied by Chibnall and Westall to the determination of glutamine in the presence of asparagine. For the determination of glutamine (+asparagine) in citrus juices by formol titration, see Solarino, Ind. ital. conserve, 1938, **13**, 32. Titration constants for *d*-glutamine and *d*-isoglutamine are given by Melville and Richardson (Biochem. J. 1935, **29**, 187). For methods of separating and determining glutamine, see also Tanbock and Winterstein, Handb. Pflanzenanalyse, 1933, **4**, 190; Chem. Zentr. 1933, **11**, 3321 and Schwab, Planta, 1936, **25**, 579.

Owing to the feebly acidic character of glutamine, very few salts have been isolated: the copper derivative,  $\text{Cu}(\text{C}_6\text{H}_5\text{O}_2\text{N}_2)_2$ , forms bluish-violet crystals, the cadmium derivative,  $\text{Cd}(\text{C}_6\text{H}_5\text{O}_2\text{N}_2)_2$ , fine prisms. Glutamine forms a compound with tartaric acid, that separates in large transparent crystals (Schulze and Godet, *l.c.*). Phenylacetylglutamine has  $[\alpha]_D^{19}$  –18° in 2–4% aqueous solution; the specific rotation decreases in acid solution (Thierfelder and Sherwin, Z. physiol. Chem. 1915, **94**, 1). *N*-chloroacetylglutamine forms needles from ethyl acetate, m.p. 130–132° and has  $[\alpha]_D^{19}$  –104° in water. For a description of dipeptides and tripeptides containing glutamine, see Thierfelder and von Cramm, *l.c.*; also Abderhalden and Spinner, Z. physiol. Chem. 1919, **107**, 1.

#### *d*-iso-Glutamine,

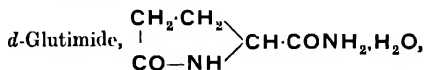


has been synthesised by Bergmann and Zervas (Ber. 1932, **65** [B], 1192) by converting the *N*-carbenzyloxy derivative of *d*-glutamic acid,

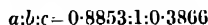


(m.p. 120°,  $[\alpha]_D^{19}$  –7.1° in acetic acid) into the anhydride (m.p. 94°) and so to the half amide, *N*-carbenzyloxy-*d*-isoglutamine, m.p. 175°, which on catalytic hydrogenation gives *d*-isoglutamine,  $[\alpha]_D^{22}$  +21.1° in alcohol. It is soluble in water but very sparingly so in organic solvents.

By the action of alcoholic ammonia on the ester of *d*- or *l*-glutamic acid, the amide of the corresponding pyrrolidonecarboxylic acid is formed; these are called *glutimides* by Menozzi and Appiani, and the *d*-, *l*- and *dl*-forms have been described.

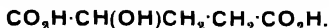


crystallises in needles belonging to the anorthic system,  $a:b:c$  1.403:1.142:1,  $\beta=86^\circ 58'$ ; it has m.p. 165° and  $[\alpha]_D^{20}$  +41.29°. *l*-Glutimide has  $[\alpha]_D^{20}$  –40° and has the same mp and other properties as its dextro-isomer. *dl*-Glutimide is formed when *l*-glutimide is heated with alcoholic ammonia at 140–150°, or alone at 200°; it has m.p. 214° (220–221°), the hydrochloride crystallises in the orthorhombic system,



(Menozzi and Appiani, Atti. R. Accad. Lincei., 1892, **7**, i, 33; Gazzetta, 1894, i, **24**, 370).

M. A. W.

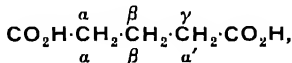
GLUTANIC ACID, *α*-hydroxyglutaric acid.

(1) *D*- $\alpha$ -Hydroxyglutaric acid, m.p. 72° (from ether),  $[\alpha]_D^{20} +1.76^\circ$ , occurs in sugar-beet molasses (see Lippmann, Ber. 1882, 15, 1156; 1891, 24, 3301), is formed by the hydrolysis of *l*- $\alpha$ -chloroglutaric acid (E. Fischer and Moersch, *ibid.* 1912, 45, 2447) or in almost quantitative yield by the dismutation of methylglyoxal-acetic acid by ketoaldehyde mutase from top-yeast (Neuberg and Collatz, Biochem. Z. 1930, 225, 242), by the enzyme from germinating peas (Mayer, *ibid.* 1931, 233, 361), by animal gly-oxalase (S. Fujise, *ibid.* 1931, 236, 237) or by the action of *B. coli* (S. Veibel, *ibid.* 1931, 232, 435).

(2) *L*- $\alpha$ -Hydroxyglutaric acid, from *D*-glutamic acid by  $\text{HNO}_3$  at  $-7^\circ$ , has m.p. 72-73° (Fischer, *l.c.*). Na salt  $[\alpha]_D^{10} -8.65^\circ$ .

(3) *DL*- $\alpha$ -Hydroxyglutaric acid is isolated as Zn salt ( $+3\text{H}_2\text{O}$ ) from the products of the action of  $\text{MnO}_2$  on synthetic glutamic acid (Wolff, Annalen, 1890, 260, 12).

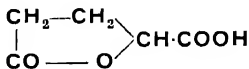
## GLUTARIC ACID,



occurs naturally in the juice of unripe sugar-beet and in the wash-water of crude wool. It is best prepared in the laboratory by the acid hydrolysis of trimethylene cyanide (Reboul, Ann. Chim. Phys. 1878, [v], 14, 501; Marvel and Tuley, Organic Syntheses, 1925, 5, 69) or of methylenedimalonic ester (Knoevenagel, Ber. 1891, 27, 2346; Dressel, Annalen, 1890, 256, 176; Otterbacher, Organic Syntheses, 1930, 10, 58) or by the oxidation of cyclopentanone with dilute nitric acid (Hentschel and Wislicenus, Annalen, 1893, 275, 315; Bødtker, J. Pharm. Chim. 1932, [viii], 15, 225).

Glutaric acid crystallises in large monoclinic plates, m.p. 97-98°, b.p. 200°/20 mm. It is readily soluble in water (100 c.c. dissolve 63.9 g. at 20°; Lamouroux, Compt. rend. 1899, 128, 999) and in alcohol and ether. For the separation of glutaric acid from succinic, adipic and pimelic acids, see Bouveault, Bull. Soc. chim. 1898, [iii], 19, 562.

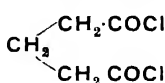
When aqueous solutions of glutaric acid are evaporated at 100° and the resulting syrup allowed to crystallise over  $\text{H}_2\text{SO}_4$ , butyrolactone- $\gamma$ -carboxylic acid is formed, m.p. 49-50°



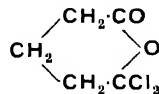
Ethyl butyrolactonecarboxylate is formed by the action of epichlorhydrin on ethyl sodium-malonate. Colourless oil, b.p. 175/25 mm. (Traube and Lehmann, Ber. 1901, 34, 171).

*Dimethyl* (b.p. 93.5-94.5°/13 mm.) and *diethyl glutarate* (b.p. 103-104°/7 mm.) are obtained by esterifying the acid with the respective alcohols hydrogen chloride (Meerburg Rec., trav. chim. 1899, 18, 373; Reboul, *l.c.*, p. 505). When the acid is heated with acetyl chloride it yields the

*anhydride* in needles, m.p. 56-57 (Mol. Rec. trav. chim. 1907, 26, 381). On heating, ammonium glutarate is converted into *glutaramide*, m.p. 152°. With phosphorus pentachloride or thionyl chloride, glutaric acid yields *glutaryl chloride*, b.p. 107-108°/16 mm. (Reboul, *l.c.*, p. 504; Ruggli, Annalen, 1913, 399, 179) which reacts as a mixture of the straight-chain form (*a*) and the cyclic form (*b*),



(a).



(b).

(Plant and Tomlinson, J.C.S. 1935, 856). For purposes of identification the following derivatives (in addition to the anhydride and imide) may be used: *amide*, m.p. 175°; *anilide*, m.p. 126-127°; *p-toluidide*, m.p. 218°; *p-phenyl-phenacyl ester*, m.p. 152°; *p-nitrobenzyl ester*, m.p. 69°.

**Halogenoglutaric Acids.**—*α*-Chloroglutaric acid is obtained by the action of sodium nitrite on the hydrochloride of  $\alpha$ -aminoglutaric (glutamic) acid; it is a solid, m.p. 97-100° (Jochem, Z. physikal. Chem. 1900, 31, 124). *Ethyl α-bromoglutarate*, b.p. 142°/11 mm., is obtained by directly brominating glutaryl chloride and pouring the product into alcohol (Perkin and Tattersall, J.C.S. 1905, 87, 366; Ingold, *ibid.* 1921, 119, 316). *β*-Bromoglutaric acid, m.p. 139-140°, is obtained by the direct addition of hydrogen bromide to glutaric acid (Semenow, J. Russ. Phys. Chem. Soc. 1912, 31, 389).

Dibromination of glutaric acid (as its chloride) yields a mixture of the two stereoisomeric *αα'*-dibromoglutaric acids (Auwers and Bernhardt, Ber. 1891, 24, 2230; Ingold, J.C.S. 1921, 119, 316; Ing. and Perkin, *ibid.* 1925, 127, 2387). the *meso*-acid melts at 170° and forms a solid *dimethyl ester*, m.p. 45°, whereas the *dl*-acid, m.p. 142°, forms a liquid *dimethyl ester*, b.p. 143-145°/10 mm. Only one of the two possible *αβ*-dibromoglutaric acids is known; this form, m.p. 157°, is obtained by the direct addition of bromine to glutaric acid (Verkade and Coops, Rec. trav. chim. 1920, 39, 586).

**Alkyl Derivatives.**—*α*-Methylglutaric acid, m.p. 79°, is best obtained by the acid hydrolysis of ethyl propene- $\alpha\gamma\gamma$ -tricarboxylate (Auwers, Annalen, 1896, 292, 210; Mellor, J.C.S. 1901, 79, 128) and has been resolved, the *d*-acid, m.p. 81°, having  $[\alpha]_D^{20} +20^\circ$  in water (Bernier and Leonardsen, Kgl. Norske Videnskab. Selskabs. Forh. 1935, 7, 125). *β*-Methylglutaric acid, m.p. 86°, is obtained by acid hydrolysis of the Michael addition product from ethyl malonate and ethyl crotonate (Auwers, Ber. 1891, 24, 308; Auwers, Kobner and von Meyenburg, *ibid.* 2888).

*αα*-Dimethylglutaric acid, m.p. 85°, is best prepared by heating *αα*-dimethylbutyrolactone with potassium cyanide in a sealed tube at 270° and hydrolysing the product with alkali (Blanc, Bull. Soc. chim. 1905, [iii], 33, 886). *ββ*-Dimethylglutaric acid, m.p. 101°, is obtained by the hydrolysis of the cyano-imide formed by

condensation of ethyl cyanoacetate with acetone in the presence of alcoholic ammonia (Guareschi, Atti R. Accad. Sci. Torino, 1901, [ii], 50, 235; Kon and Thorpe, J.C.S. 1919, 115, 694; Vogel, *ibid.* 1934, 1758), this process may be extended to the preparation of the  $\alpha\beta$ -trialkylglutaric acids (Kon and Thorpe, *ibid.* 1922, 121, 1795) or by the hypobromite oxidation of dimethyl-dihydroresorcinol (Komppa, Ber. 1899, 32, 1423; Walker and Wood, J.C.S. 1906, 89, 599).  $\alpha\beta$ -Dimethylglutaric acid, m.p. 87°, is obtained by hydrolysis of the corresponding imide (Thorpe and Young, *ibid.* 1903, 83, 357).  $\alpha\alpha'$ -Dimethylglutaric acid is obtained (i) by the action of methylene iodide on ethyl sodio- $\alpha$ -cyanopropionate, followed by acid hydrolysis of the resulting cyano-ester (Zelensky, Ber. 1899, 22, 2823), (ii) by hydrolysis and decarboxylation of ethyl  $\alpha\alpha'$ -dimethyl- $\alpha$ -cyanoglutarate (Howles, Thorpe and Udall, J.C.S. 1900, 77, 949) and (iii) by acid hydrolysis of the condensation product from ethyl methylmalonate and ethyl  $\alpha$ -methylacrylate or ethyl  $\alpha$ -bromoisobutyrate (Auwers and Jackson, Ber. 1890, 23, 1611; Auwers and Thorpe, Annalen, 1895, 285, 310; Auwers and Kobner, Ber. 1891, 24, 1936). The *meso*-, m.p. 128°, and *racemic*-, m.p. 143°, forms may be separated by treatment of the mixture with acetyl chloride, whereby the latter is converted into the anhydride. (*See also CARBOXYLIC ACIDS.*)

H. N. R.

GLUTEN (*v.* Vol. II, 84c).GLUTENIN, GLUTELIN (*v.* Vol. II, 856c)."GLUTOLIN" (*v.* Vol. II, 480a).

GLYCERIC ACID,

HO·CH<sub>2</sub>·CH(OH)CO<sub>2</sub>H.

*dl*-Glyceric Acid is prepared by the action of fuming nitric acid (1 part) on a 50% aqueous solution of glycerol (2 parts). The acid is separated from the products of the reaction in the form of the lead or calcium salt and isolated by treatment of these salts with hydrogen sulphide or oxalic acid respectively (Debus, Annalen, 1858, 106, 80; Beilstein, *ibid.* 1861, 120, 229; Moldenhauer, *ibid.* 1864, 131, 324; Mulder, Ber. 1876, 9, 1902; Böttinger, *ibid.* 1877, 10, 267; Rosenthal, Annalen, 1886, 233, 16; Meyer, Ber. 1886, 19, 3294; Lewkowitsch, *ibid.* 1891, 24, Ref. 653; Wohlf, J. pr. Chem. 1900, [ii], 61, 209). Also prepared, together with other products, by the action of air or H<sub>2</sub>O<sub>2</sub> on an alkaline solution of glucose (Glatfield, J. Amer. Chem. Soc. 1929, 50, 151; *cf.* Nef, Annalen, 1914, 403, 217). Glyceric acid forms a thick syrup, soluble in water and alcohol but insoluble in ether.

*Methyl ester* has b.p. 119–120°/14 mm.,  $d_{15}^{20}$  1.2814. *Ethyl ester* has b.p. 120–121°/14 mm.,  $d_{15}^{20}$  1.1909 (Frankland and McGregor, J.C.S. 1893, 63, 512).

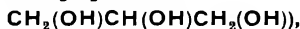
*d*-Glyceric Acid. The calcium salt is obtained from the corresponding salt of the *dl*-acid by the action of *B. ethaceticus* (Frankland, *et al.*, J.C.S. 1891, 59, 97; 1893, 63, 296); of *P. glaucum* (Lewkowitsch, Ber. 1883, 16, 2720; McKenzie and Harden, J.C.S. 1903, 83, 431);

or by the action of *A. niger* and *A. griseus* on *dl*-glyceric acid (Mackenzie and Harden, *l.c.*); also by the fractional crystallisation of the brucine salts formed by the *dl*-acid (Frankland and Done, *ibid.* 1905, 87, 622). The aqueous solution of the acid is dextrorotatory, the salts are levorotatory and more soluble in water than those of the *dl*-acid.

The *methyl ester* has b.p. 119–120°/14 mm.,  $d_{15}^{15}$  1.2799,  $[\alpha]_D^{15}$  –4.80°, the *ethyl ester* has  $d_{15}^{15}$  1.1921,  $[\alpha]_D^{15}$  –9.18° (Frankland and McGregor, *ibid.* 1893, 63, 511). The *amide* forms plates or prisms, m.p. 99.5–100°,  $d_4^{100}$  1.3347,  $[\alpha]_D^{100}$  39.98° (Frankland, Wharton and Aston, *ibid.* 1901, 79, 269).

*l*-Glyceric Acid, prepared by the action of milk of lime on glucuronic acid (Neuberg and Silbermann, Ber. 1904, 37, 339). The salts are dextrorotatory, the *barium* salt having  $[\alpha]_D +17.1^\circ$ .

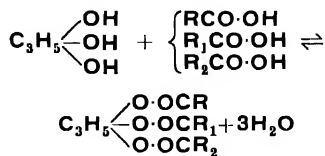
GLYCERIN (Glycerol;  $\alpha\beta\gamma$ -trihydroxypropane; 1:2:3-propanetriol,



a trihydric aliphatic alcohol occurs in combination with fatty acids as esters or "glycerides" in all fatty oils and fats. Glycerin was discovered by Scheele (Crell's Chem. J. 1779, 4, 190; Crell's Chem. Ann. 1784, 1, 99) in the course of studies on the action of litharge on olive oil (preparation of "lead plaster") and other fatty oils, and termed by him *principium dulce oleorum*.

The name *glycerin* (from the Greek γλυκερός, sweet), later modified to *glycerol*<sup>1</sup> in conformity with the usual nomenclature for alcohols, was conferred upon it by Chevreul, who recognised it as an essential and characteristic component of the fats, and pointed out the nature of its association with the fatty acids therein.

The composition of glycerol was ascertained by Pelouze (Ann. Chim. Phys. 1836, [ii], 63, 19; Compt. rend. 1845, 21, 718) and its constitution was finally established by the work of Berthelot (Ann. Chim. Phys. 1854, [iii], 41, 216) and of Wurtz (Compt. rend. 1857, 44, 780; Annalen, 1857, 102, 339) and confirmed by its synthesis by Friedel and Silva (Compt. rend. 1872, 74, 805; 1873, 76, 1594) and by Piloty (Ber. 1897, 30, 3161). The fatty oils and fats consist essentially of *glycerides*, the esters formed by the combination of fatty acids with glycerol with the elimination of 3 mol. of water, as expressed by the following equation:



in which RCO·, R<sub>1</sub>CO·, R<sub>2</sub>CO· represent radicals of fatty acids, which may be all alike, or derived from different fatty acids.

<sup>1</sup> In view of the common usage of the trivial name *glycerin*, it is convenient to retain this to denote the ordinary technical or commercial material, and to reserve the term *glycerol* for the pure chemical.



If the three fatty acid radicals are identical, the ester is known as a *simple triglyceride*; if, however, the three hydrogen atoms are replaced by two or three different fatty acid residues, then *mixed glycerides* are obtained.

It was formerly assumed that the natural fats consisted of mixtures of simple triglycerides, and (erroneous) references to the presence of simple glycerides such as tristearin, triolein, tripalmitin, etc., are common in the older literature. Modern researches, however, and especially those of Hilditch and his pupils (*cf.* T. P. Hilditch, "The Chemical Constitution of the Natural Fats," London, 1940) have shown that simple triglycerides rarely occur in more than very small amounts in natural fats (particularly so in seed-fats), and that most of these are composed chiefly of "mixed triglycerides," such as oleo-dipalmitin, palmito-oleo-stearin, oleo-distearin, etc. (*cf.* Table XVIII). The seed fats of laurel and of nutmeg, which contain some 30% of trilaurin and 40% of trimyristin respectively, are remarkable.

The equation shown above, when read from right to left, symbolises the *hydrolysis* or *saponification* of fats and expresses the fact that by the addition of the elements of water (which is usually effected with the assistance of suitable catalysts), neutral glycerides may be resolved into 3 mol. of fatty acid and 1 mol. of glycerol.

Glycerol exists solely in the combined state in fresh natural fats and oils, although traces of the free alcohol may be found occasionally in fats which have suffered a certain amount of deterioration from hydrolysis. Free glycerol is to be found in small amounts in the blood and is also a constant product of the alcoholic fermentation of sugar (Pasteur, *Compt. rend.* 1858, 46, 857; 47, 224; 100 parts of sugar yield about 3.5 parts of glycerol under the ordinary conditions of fermentation. Until the beginning of the century, such a source of glycerol was of no commercial interest, but later the increasing value of glycerol made it profitable to recover even this small proportion and various processes were devised to treat the *vinasses* from distilleries for this purpose.

For example, in Barbet's process (F.P. 449961 of 1912) the material is concentrated, mixed with calcined plaster and kieselguhr, and the glycerol distilled under reduced pressure, while caramelisation is prevented by the action of scrapers within the retort. In another process (B.P. 27300 of 1912) the *vinasses* are dried, treated with acid, and the glycerol extracted by means of solvents such as alcohol.

A great advance was made as a result of the investigations of C. Neuberg (*cf.* papers in *Biochem. Z.* 1913-21; *Ber.* 1919-20; *Biochem. Z.* 1929, 216, 233) and of Connstein and Lüdecke, who showed that the course of the fermentation of sugar could be modified and the production of glycerol (at the expense of alcohol) be greatly increased by conducting the fermentation in the presence of sodium sulphite in an alkaline medium (*v.* FERMENTATION, ALCOHOLIC, Vol. V, 23d, 24ab). These researches led to the development by Connstein and Lüdecke (*Ber.* 1919, 52, 1385; J.S.C.I. 1919, 287a) of a process for the industrial production of glycerol by the fermentation of

beet sugar, which was worked by the Protol Gesellschaft in Germany and Austria during the war of 1914-18, some 1,000 tons per month of glycerol being manufactured by this method (*cf.* Connstein and Lüdecke, and/or Vereinigte Chem. Werke, G.P. 298593-6, 343321, 347604, 86699, 514395; B.P. 138099, 138328-9, 38331; U.S.P. 1511754, 1698800). For the theory of the sulphite-modified and alkaline fermentation of sugar, *cf.* references quoted above; Tomoda, *J. Chem. Ind. Japan*, 1924, etc.; *Proc. World's Eng. Congress*, Tokyo, 1929; 1931, 31, 500; FERMENTATION, ALCOHOLIC, *l.c.*

Still higher yields of glycerol, corresponding almost to the theoretical yield to be expected from Neuberg's second equation, are stated to be obtained when fermentation is performed in the presence of a mixture of neutral and acid sodium sulphites in such proportion as to be approximately neutral to litmus (Cocking and Lilly, B.P. 164034/1919; Lilly and I.C.I., Ltd., B.P. 349192/1930; *cf.* K. and N. Lüdecke, B.P. 278086/1926).

In the United States also, the processes of alkaline fermentation attracted attention to the possibility of fermenting blackstrap molasses: thus Koff, Lander and Beyer (*J. Ind. Eng. Chem.* 1919, 11, 842; U.S.P. 1288398/1918; B.P. 133374; F.P. 499824), using pure cultures of *Saccharomyces ellipsoideus* var. Steinberg in an alkaline mash, obtained a conversion of 20-25%. If the sugar into glycerol as well as considerable production of alcohol. Further processes for the production of glycerol by the alkaline fermentation of crude sugar have been patented by E. I. Du Pont de Nemours & Co.; *v.* U.S.P. 1678150, 1725363, 1936497, 1990908; B.P. 316567, 316597.

Interest in the fermentation processes for the production of glycerol, which tends to lapse in normal peace-time in consequence of the plentiful supplies of cheap glycerol from fats, may be expected to revive in time of war, when a shortage of glycerol for the manufacture of explosives is experienced; and in fact, such processes have again been brought into use in Germany at the present time.

The manufacture of *synthetic glycerol* from propylene, which can be obtained from the unsaturated gases produced during the cracking of petroleum, may also become of commercial interest in times of shortage. A patent issued to Heinemann (U.S.P. 1180497; B.P. 12366/1913) claimed the conversion of propylene through the stages of dichloropropane and allyl chloride into trichloropropane, which was then hydrolysed to glycerol (*cf.* McElroy (Carbide and Carbon Chemicals Corp.), U.S.P. 1466665; E. C. Williams, *Oil and Gas J.* 1938, 37, 28). The conversion of propylene into glycerol may also be effected by making use of the chlorohydrin derivatives as intermediate steps (*cf.* McElroy (Chemical Development Co.), U.S.P. 1253615; Essex and Ward (Du Pont de Nemours & Co.), U.S.P. 1477113, 1594608).

The various stages in the process recently worked out on the technical scale by the Shell Development Co. have been outlined by E. C. Williams (*Chem. Met. Eng.*, 1940, 47, 834).

Propylene is chlorinated directly at a temperature of 500°C. (the so-called "hot chlorination process," cf. Groll and Hearn, *Ind. Eng. Chem.* 1939, **31**, 1530) to yield allyl chloride, from which the synthesis of glycerol may proceed by either of two routes. Thus allyl chloride may be treated with caustic soda at a controlled pH of 8-11 to convert it into allyl alcohol: this reacts with aqueous hypochlorous acid to form glycerol mono- and di-chlorohydrins, which in turn are hydrolysed by a solution containing 10% of caustic soda and 1% of sodium carbonate to yield glycerin. The alternative method (which appears to be preferable for large scale production) is to chlorohydrinate the allyl chloride directly, by treating it with a solution of hypochlorous acid and sodium chloride (prepared by the action of chlorine on caustic soda solution) so as to obtain glycerol dichlorohydrin (in 90-95% yield), which is then hydrolysed to glycerin by the aid of caustic soda or caustic soda and lime. The crude glycerin synthesised by such methods is concentrated and distilled: by taking appropriate cuts during the distillation, and refining them by extracting coloured impurities with xylene (*c.* Shell Development Co., U.S.P. 2154930) and redistilling, a glycerin meeting all commercial specifications may be recovered in high yield.

Laboratory preparations of glycerol from propylene (itself synthesised from acetylene) *via* tribromopropane or trichloropropane have been described by Berthelot (*l.c.*) and Wurtz (*l.c.*). Allyl alcohol may be oxidised to glycerol by means of potassium permanganate (Wagner, *Ber.* 1888, **21**, 3347, 3351), or by potassium chlorate in the presence of osmium tetroxide as catalyst (Hofmann, Ehrhart and Schneider, *ibid.* 1913, **46**, 1657, 1667).

Glycerol may likewise be prepared from propane, which itself may be recovered from petroleum.

*Crude glycerin* is obtained on the large scale from fats and oils as a by-product of soap-making and of the various saponification processes (fat-hydrolysis) practised in soap and candle works for the manufacture of fatty acids. According to the process by which the fat is hydrolysed, the following five commercial qualities of glycerin have been distinguished hitherto, viz.: (1) *Soap-Lye Glycerin*, or *Soap Crude Glycerin*; (2) *Saponification Crude Glycerin*; (3) *Twitchell Crude Glycerin*; (4) *Crude Distillation Glycerin*; and (5) *Fermentation Crude Glycerin* (*N.B.* this refers to the glycerin obtained by hydrolysing fats by the help of enzymes or ferments, and not to glycerin obtained from the fermentation of sugars). In view of potential developments discussed above, crude glycerin derived from the fermentation of sugar and, perhaps, also synthetic crude glycerin should be added to complete the list of crude glycerins from all sources. Typical analyses of some crude glycerins are shown in Table I.

In the soap and stearine industries, the by-product glycerin is obtained as a dilute aqueous solution (soap lyes or "sweet waters"), containing various impurities, viz., salts, inorganic and/or organic acids and other organic sub-

stances—the nature and quantity of which depend upon the manufacturing processes themselves—and which must be removed as far as possible before the liquors can be concentrated by evaporation to obtain commercial crude glycerin. The method employed depends naturally upon the type of impurity to be eliminated.

The organic contaminants, which although small in quantity may cause considerable difficulties in the processing, may arise from the use of low-grade, impure or deteriorated fats for saponification. The purest raw material results from saponification by means of lime in open vessels; hardly inferior to this is the glycerin obtained by "autoclaving." Less pure is the raw material recovered from the "acid saponification process," "Twitchell's process," and the "ferment process." The crude glycerin obtained from soap lyes, notwithstanding its high proportion of inorganic salts, may, on the one hand, surpass in purity (*i.e.* as regards the amount of organic impurities) the crude material from the last-named processes; but, on the other hand, it may be very impure if fats and oils of low quality have been saponified by means of black-ash lyes, as was done until some years ago in Lancashire and in Marseilles. Modern processes of refining have, however, overcome a number of difficulties caused by the several impurities, so that to-day a chemically pure glycerol from good soap lyes cannot be distinguished from chemically pure glycerol obtained by lime saponification. Crude glycerins further vary as regards quality in accordance with the care exercised in the manufacture. Crude glycerins obtained from the acid saponification, the Twitchell and the ferment processes, retain tenaciously certain impurities and are therefore rather more difficult to purify.

(1) *Soap-Lye Glycerin, Soap Crude Glycerin, Soap Crude.*—Since Chevreul established the constitution of fats and oils, it has been known that the spent soap lyes, obtained in the manufacture of soap by boiling oils and fats in an open pan with caustic soda, contain practically all the glycerol which the natural oils and fats are capable of yielding. During the first half of last century, however, no attempt was made to recover the glycerol from those lyes, not only on account of the difficulty attending this operation, but also for the reason that the small demand for glycerin then ruling in the market could be readily satisfied by the candle makers' crude glycerin. When, at the end of the 'seventies of the last century, a great demand for nitroglycerin (*dynamite*) sprang up, attention was drawn to this source of glycerin, and serious endeavours were made to recover the hitherto wasted product. Although as early as 1858, H. Reynolds had patented (B.P. 1322) the main features of a process of recovery, features which essentially reappeared in all subsequent processes, yet serious failure at first attended all attempts at the recovery of glycerin, on account of the considerable amount of impurities in the spent lyes, and most prominently on account of the large amount of dissolved salts. The first process to achieve successful technical production of crude glycerin from soap lyes was

patented in 1879 by Thomas, Fuller and King (B.P. 1282). Modern processes, especially improvements in apparatus on the one hand, and the rapidly growing employment in the soap industry of caustic soda of the highest purity, tended to evolve a process which is now worked with more or less success in all the large soap works, not only of Europe and America, but also of Australia, Africa, India and New Zealand. The earliest successful attempts to recover glycerin from soap lyes were made in English soap works, which were the largest soaperies of the world; this process may be said to have established its success in Great Britain towards the middle of the 'eighties of the last century. Since that time, crude glycerin recovered from soap lyes, "soap crude glycerin," has established its great importance in the world's commerce.

According to the manner in which the soap is processed, the spent lyes contain from 5 to 8% of glycerol, also the common salt used in "cutting" or "graining" (*i.e.* salting-out) the soap, and small amounts of free caustic soda, sodium carbonate, soap and organic impurities. The smaller the amount of free caustic soda, sodium carbonate and organic impurities present, the more readily can the process of recovery and purification be carried out. In cases where impure caustic soda lyes have been used, the spent soap lyes may contain, in addition to the substances enumerated above, thiocyanates, sulphides, thiosulphates, cyanides, and ferro-cyanides. These impurities were present in the crude (black-ash) lyes which were at one time used in the Marseilles district. The difficulties caused thereby in the recovery of crude glycerin, coupled with the establishment of Solvay's soda works in that neighbourhood, led to the almost complete abandonment of black-ash lyes, so that even in Marseilles the vast majority of soaps are now prepared with pure caustic lyes. The exact treatment of the lyes in a soap works depends on the state of purity of these lyes, and has, as its object, the removal or destruction of the soapy, resinous, albuminous and mineral impurities present, so that the final dilute glycerin liquors passing to the evaporators shall contain practically no impurity other than common salt.

This is achieved by first separating any undecomposed fat, then very carefully acidifying with hydrochloric acid to decompose traces of soap, and adding ferric chloride (or less commonly aluminium sulphate) until no further precipitation takes place. (Formerly iron sulphate was much used, *cf.* Van Ruyambeke, U.S.P. 458647; G.P. 86563). The liquor is then filter-pressed, made alkaline to precipitate any excess of iron and again filter-pressed. Other methods (*cf.* Schlenker, Chem. Umschau, 1932, 39, 28) involving the use barium carbonate and other salts have been proposed but are not much used on the large scale.

If "chemically pure" glycerin is subsequently to be prepared from the crude product, attention must be paid to the elimination of arsenic compounds, and arsenic-free reagents should be employed for the purification of the lyes. A. C. Langmuir (Ind. Eng. Chem. 1932, 24, 378) states that simple treatment with crude

ferric sulphate and filtration is sufficient to remove arsenic from spent lyes. The removal of arsenic from concentrated glycerin solutions is more troublesome (*v. infra*, "C.P. Glycerin").

The chief difficulty attending the concentration of the purified soap lyes arises from the high content of common salt; for, unless special arrangements are made, the salt is liable to crystallise out as a deposit on the walls and in the tubes of the evaporator, reducing its working efficiency and necessitating frequent stoppages for cleaning.

In the early days of the industry, the concentration of the purified glycerin liquors was carried out in fire- or steam-heated open pans of conical shape, so that the salt, as it crystallised, could slide down into a vessel fixed to the bottom of the pan, whilst rotating gear kept the heating surface free from incrustation. In the case of large and modern installations, the lyes are evaporated, usually under reduced pressure, with the help of steam in single- or multiple-effect closed evaporators of special design. The *Foster double-effect* evaporator, illustrated in Fig. 1 (*cf.* Foster, B.P. 3118/1895, 23681/1899, 26836/1902), which is most commonly used in England, is a typical example of such apparatus. The glycerin liquors are heated as they circulate from the conical bottom of the evaporator up through a number of narrow tubes located in the calandria or steam-chest into the vapour zone or evaporation space proper, where some of the water volatilises; thence the liquors return for recirculation to the bottom of the vessel through the wide downcomer which is a notable feature of all such evaporators, and facilitates the rapid circulation of the lyes. Various other patented evaporators—such as the *Scott* and the American *Wurstler-Sanger, Garrigue* and *Buflavak* evaporators—differ in details of construction,<sup>1</sup> but embody similar principles, the object of the design being to achieve a rapid, positive circulation of the lyes without churning, so that a high rate of heat transfer and evaporation is attained, and the separating salt crystals are able to grow freely and to settle down on the bottom of the evaporator, whence they are withdrawn continuously or intermittently by suitable salt-extractors or salt-drums, without breaking the vacuum in the evaporator.

In the *Blair, Campbell and McLean* system, the lyes are heated under pressure (so that no salts are deposited in the tubes), and the actual evaporation is produced by "flash" effect in a separate vessel remote from the source of heat.

The well-known *Kestner climbing-film* evaporator has also been adapted for concentrating glycerin by the provision of a salt-separating vessel through which the liquors flow after each passage up the tubes of the evaporator (*v. EVAPORATION*, Vol. IV, p. 410b); as a rule, two or four evaporating units are coupled with one salt-separating vessel.

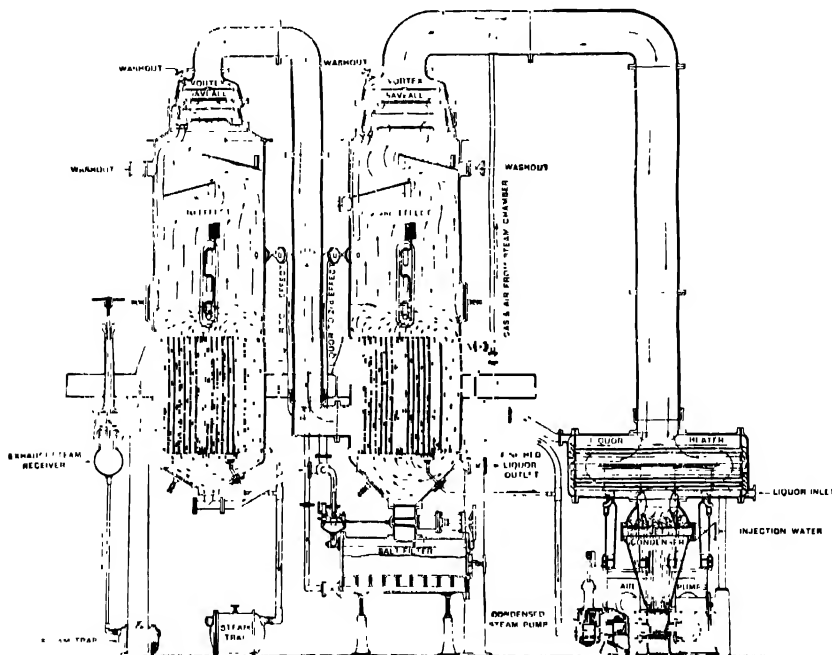
<sup>1</sup> The various English and American evaporators are illustrated, and their operation described in some detail by E. T. Webb, "Soap and Glycerine Manufacture," London, 1927; G. Martin, "Modern Soaps and Detergent Industry," Vol. III, London, 1925; and by J. W. Lawrie, "Glycerol and the Glycols," New York, 1928.

The collected salt sludge is ultimately filter-pressed or centrifuged, and washed with purified dilute glycerin lyes in order to recover any entrained glycerin. The salt itself is recovered in a sufficient state of purity to be returned to the soapery.

The glycerin solutions are concentrated until the crude glycerin has reached a sp.gr. of 1.3. The progress of concentration is controlled by the sp.gr. test, or, equally well, by taking out samples and ascertaining the boiling-point in a porcelain dish, by means of a thermometer, while the contents of the dish are kept stirred, so that the salt may not cause bumping of the contents or cracking of the dish. The glycerin has reached the sp.gr. of 1.3 and the percentage

required by commerce, if the boiling-point is 150°. The crude glycerin then contains 80% of pure glycerol, and about 10% of salts, the remainder consisting of water and a small amount of organic impurities. If the concentration is carried a little further, crude glycerin, containing as much as 86% of glycerol, can readily be obtained.

The proportion of organic impurities in soap-lye glycerin varies considerably, depending on the process of purification and the care of the operator. Some commercial "soap crude" glycerins contain less than 1% of organic impurities (thus representing a better quality glycerin than "crude distillation glycerin," crude glycerin from the "Twitchell process," and crude gly-



[By courtesy of Fullerton, Hodgart and Barclay, Limited, Paisley.

FIG. 1.—Section of Foster's patent Evaporator.

cerin from the "fermentation process"). Other specimens of crude glycerin, again, contain large quantities of impurities, consisting of fatty acids, rosin acids, and of albuminoid substances, gelatin and hydrocarbons (from bone fat), and also trimethyleneglycol in the lyes resulting from bone fat which have been allowed to ferment. Even organic bases, amongst which picoline and lutidine were identified, have been found in the distillates from such impure glycerins (Lewkowitsch, "Oils, Fats and Waxes," 6th ed., 1923, Vol. III, 385.

The colour of "soap crude glycerin" is pale-yellow to brown, or almost black, according to its purity. The taste of good "soap crude" is sweet, modified, of course, by that of the com-

mon salt contained therein. Impure samples have a most unpleasant garlic-like taste, even if sulphides be absent. This is specially characteristic of the lyes obtained in the Marseilles district, owing to the use of "sulphur" olive oil.

Soap-lye glycerin can be rapidly distinguished from the crude glycerins described below by the large proportion of common salt which it contains (heavy precipitate with silver nitrate solution) and by its high specific gravity.

Crude soap-lye glycerin, if containing considerable quantities of sulphides, thiosulphates or sulphites, is almost valueless to the refiner of crude glycerin.

Table I illustrates the composition of recent soap-lye and saponification crude glycerins.

TABLE I.

## SOAP-LYE CRUDE GLYCERIN.

	1.	2.	3.	4.	5.
Sp.gr. at 15.5° . . . . .	1.3016	1.2994	1.2971	1.3062	1.3073
Total acetyl value . . . . .	83.38	81.66	82.72	84.91	87.24
Acetyl value of residue . . . . .	—	0.66	0.51	2.39	1.01
Net glycerol . . . . .	—	81.00	82.21	82.52	86.23
Ash . . . . .	9.45	9.40	9.25	9.51	8.88
Organic residue . . . . .	1.56	2.97	1.25	3.16	1.29
Water . . . . .	5.79	5.50	7.01	4.90	3.24
	100.18 <sup>1</sup>	98.87	99.72	100.09	99.64

## SAPONIFICATION CRUDE GLYCERIN.

	1.	2.	3.	4.	5.
Sp.gr. at 15.5° . . . . .	1.2517	1.2447	1.2516	1.2579	1.2472
Total acetyl value . . . . .	90.18	88.57	86.06	91.85	90.88
Acetyl value of residue . . . . .	0.20	—	0.73	0.31	—
Net glycerol . . . . .	89.98	—	85.33	91.54	—
Ash . . . . .	0.97	0.83	2.47	1.39	0.47
Organic residue . . . . .	1.36	0.48	2.72	1.13	0.33
Water . . . . .	7.55	10.05	9.24	5.82	8.34
	99.86 <sup>1</sup>	99.93	99.76	99.88	100.02

<sup>1</sup> When the organic residue of soap crude glycerin is less than 2.5% it is customary in the trade not to determine the acetyl value of the residue. In such cases the sum of total acetyl value, ash, organic residue and water will usually be a little over 100. When the acetyl value of the residue is determined and deducted so as to arrive at net glycerol the sum will usually be a little less than 100. In the case of saponification crude glycerin the acetyl value of a residue less than 1% is not usually determined (*see p. 62b*).

(2) **Saponification Crude Glycerin.**—This product represents the best quality of crude glycerin. It is recovered from the "sweet waters" of the autoclave process (a process in which fats are hydrolysed with water at high temperatures and pressures in the presence of small quantities of lime, magnesia or zinc oxide as catalyst) or as a by-product from the manufacture of soap by double decomposition. (In this method the fats are completely converted into calcium soaps by treatment with excess of lime and water, and subsequently converted into sodium or potassium soaps by double decomposition with appropriate alkali salts: the glycerin liquors are washed out of the lime soaps at the end of the first step in the process.)

The proportion of glycerin in the "sweet waters" varies from about 6 to 16%. The refining of these liquors is comparatively simple, and some of the operations necessary for the treatment of soap lyes may be omitted. Preliminary purification may be effected by partial concentration over closed steam coils assisted by skimming. The liquors are then acidified with sulphuric acid, in order to decompose metallic hydroxides and soaps, and after filtering off any separated fatty acids, the solution is neutralised with lime and concentrated in single- or multiple-effect evaporators: since the purified autoclave "sweet waters" contain relatively little dissolved salts, the provision of special salt-extractors, etc.,

such as are required in dealing with soap crudes, is superfluous.

The evaporation is carried on until the crude glycerin contains about 85–90% of glycerol. Its sp.gr. is then from 1.240 upwards, corresponding with the commercial brand of "28°Bé. saponification crude" or "candle crude glycerin." The colour of this glycerin varies from yellow to dark-brown; its taste is sweet. With basic lead acetate, it gives but a slight precipitate. By refining this crude glycerin with charcoal, a "refined" glycerin (used for a number of commercial purposes) is obtained. This crude glycerin contains up to 0.3% of ash, chiefly calcium (or magnesium or zinc) sulphate, and only small quantities of organic impurities. It is valued on the percentage of pure glycerol, of ash and of organic impurities.

The "sweet water" obtained in the process of soap making by double decomposition is treated in the same manner as described above, and yields a good "saponification crude," which is equal in quality to a "candle crude glycerin," provided that the original fatty matter was of good quality. Since this process is used in small works only, where chiefly low-quality greases are worked up, the crude glycerin thus obtained may have a very high ash content and is apt to contain a considerable amount of organic impurities, so that it is liable to ferment when stored. (The experience of Lewko-

witch that such crude glycerins did ferment shows that the organic impurities in low-class greases are not destroyed by treatment with lime.) In the course of the fermentation, trimethyleneglycol is formed.

(3) **Crude Glycerin from the Twitchell and Analogous Processes.**—This kind of crude glycerin is obtained from the acid "sweet waters" resulting from the Twitchell process of fat-splitting, which consists in treating the fat with water containing a little sulphuric acid in the presence of a complex organic sulphionate as catalyst. The acid liquors are treated with baryta or barium carbonate or lime to precipitate as far as possible the dissolved sulphuric acid, after which the purification and concentration proceed as described under "saponification crude glycerin." Any dissolved calcium sulphate may be removed by precipitation with barium hydroxide or carbonate, in order to avoid complications during the evaporation. The purified liquors are concentrated up to a sp.gr. of about 1.24 or more. The quality of this crude glycerin varies considerably with the quality of the fatty material from which it has been obtained. If the raw material is of good quality, the glycerin is fairly good; but even in that case, owing to the high amount of ash it contains, and owing to its unpleasant taste, it is valued at a somewhat lower price than is crude candle glycerin. Since the Twitchell saponification process is best adapted to low-class material (such as greases), the glycerin obtained from such material contains so considerable an amount of organic impurities that it cannot be refined by itself, even for the production of dynamite glycerin. Each special make of such glycerin must therefore be valued on the basis of the impurities it contains.

(4) **Crude Distillation Glycerin.**—This kind of crude glycerin is obtained from the acid water resulting from the so-called acid saponification processes in which fats are hydrolysed with the help of sulphuric acid. It is termed in commerce "crude distillation glycerin" for the reason that the fatty acids obtained by this process must be distilled to yield candle material. The dilute glycerin waters ("sweet waters") are worked up in much the same manner as described under "Twitchell glycerin." Owing to the large amount of sulphuric acid used in the process, a considerable quantity of salts remain in solution after the mineral acid has been neutralised with lime. As the concentration of the solution proceeds, especially when the thickened liquor approaches the sp.gr. of 1.240, calcium sulphate separates out and is deposited on the heating surface of the evaporating apparatus in the form of a hard crust, thereby rapidly diminishing the evaporative power of the steam. This difficulty is obviated by employing a type of evaporator which permits the heating surface to be continuously scraped.

The finished crude distillation glycerin contains considerable proportions of calcium sulphate, inasmuch as the solubility of calcium sulphate in glycerin (*see below*) is increased by the organic impurities which are also present. The ash of this kind of crude glycerin rises to as much as 2 and even 3.5%. The amount

of organic impurities is greater than in crude saponification glycerin, and may rise to even 2%, the colour is usually pale-yellow, the taste sharp and astringent, and when rubbed between the hands it emits an unpleasant odour. On adding basic lead acetate, a voluminous precipitate is obtained; hydrochloric acid produces a turbidity, due to the presence of fatty acids.

The trade term for this kind of glycerin is "crude distillation glycerin, 28°Bé," it has sp.gr. 1.240–1.242, and as a rule contains from 84 to 86% of glycerol.

(5) **Fermentation Crude Glycerin.**—The "sweet water" from the hydrolysis of fats by means of enzymes is rich in proteins and other organic impurities. In addition to the usual treatment described above, it must be filtered over char, which retains the bulk of these impurities. Nevertheless, a certain amount is still retained and the finished crude is not only dark in colour, but has also a very unpleasant odour and taste, even if the glycerin be made from good raw material, such as refined cotton-seed oil or refined linseed oil, and in the infancy of the process this crude glycerin was practically unusable. In consequence of improvements, the amount of impurities has been considerably reduced and a sample examined by J. Lewkowitch (*op. cit.* III, 379) give the following somewhat favourable results: sp.gr. 1.2369; ash, 0.49%; organic impurities (proteins, etc.), 1.54%. But the difficulties have not yet been surmounted, and the process is still but little used. This product, like the Twitchell crude glycerin, is difficult to refine by the usual process of distillation and must be mixed in the still with better kinds of crude glycerin.

(6) **Crude Glycerin from the Fermentation of Sugars.**—The purification of the relatively dilute glycerin liquors obtained from the fermentation process presents special problems on account of the quantity and variety of the associated contaminants. After filtering the fermented mash to remove the yeast, the cleared glycerin slop may contain only from 2 to 7% of glycerol together with a wide variety of organic products of the fermentation, alkaline salts, sulphites and other inorganic salts which were originally added as nutrients for the yeast. Alcohol, aldehydes and other volatile impurities may be removed by distillation. According to Verbeek's description of the process used by the Protol Co. in Germany (Seifens.-Ztg. 1921, 47, 591, 633), this distillation was continued until the liquors reached the point of incipient crystallisation of the contained salts; the concentrated solution (containing some 14–18% of glycerol) was settled, filtered and treated with calcium chloride and calcium hydroxide to precipitate the bulk of the salts present. These were removed by filtration, and the iron and calcium salts in the filtrate were precipitated by the addition of sodium carbonate in the presence of a little solid ferrous sulphate (the calcium salts might also be precipitated as insoluble oxalate, cf. Vereinigte Chem. Werke, Altenburg and Menz, G.P. 403077), and the filtered solution was acidified with hydrochloric acid prior to the final evaporation to "crude glycerin." Even the best crudes obtained,

however, did not contain more than 60% of glycerol, and were heavily contaminated with sulphites, thiosulphates and trimethylene glycol, etc. Kellner (Z. deut. Oel- u. Fett-Ind., 1920, 40, 677) states that it was found impossible to prepare a pharmaceutical quality of glycerin from these crudes.

Improved methods for the purification and recovery of dynamite glycerin from fermented blackstrap molasses have been patented by Du Pont de Nemours & Co., U.S.P. 1626986, 1627040, 1881718, 1936497; B.P. 316567, 316597, 410782, etc.; Barbet et Fils & Cie., B.P. 168835, and crudes containing 75% of glycerin have been produced. These are, however, dark in colour and contain a considerable amount of organic impurities which tend to cause excessive foaming and other difficulties in the subsequent distillation.

(Methods for the analysis of sugar fermentation crude glycerins worked out by Cocking and Lilly, Fachihi, Lawrie and others are described by J. W. Lawrie, "Glycerol and the Glycols," London and New York, 1928, pp. 139-151).

Considerable quantities of crude glycerin, especially crude saponification glycerin, are used in the arts for various purposes (*see below*). By far the largest quantities of crude glycerin are, however, purified by distillation, and thereby converted into *distilled glycerin*. In commerce, two kinds of distilled glycerin are differentiated, *i.e.* distilled glycerin for making nitroglycerin (dynamite), *dynamite glycerin*, and *chemically pure (C.P.) glycerin*, sometimes termed *double-distilled glycerin*.

**Distilled Glycerins.**—The distillation is most commonly carried out in a vacuum. In the early days of the industry, fire-heated stills were employed which remained in use to some extent even after the introduction of steam as a carrier vapour (*cf.* Wilson and Payne, B.P. 1624/1854) and the development of processes for steam-distillation *in vacuo* (*cf.* O'Farrell, B.P. 3284/1881; Clark, B.P. 5348/1881). Some manufacturers work off a certain amount (depending on the size of the still) of crude glycerin in one batch. Other manufacturers resort to continuous distillation, the still being fed as the glycerin distils off.

The successful distillation of crude glycerin depend largely on the skill and care of the operator, and although a considerable number of special apparatus have been patented, and are still being patented, the success depends more on attention to details than on the particular apparatus employed, and the details of the *modus operandi* in conducting the distillation are considered valuable secrets.

In the *Van Ruymbeke* still (U.S.P. 458647-8/1891; B.P. 24556/1893; G.P. 86829/1896) the steam is simultaneously expanded and superheated by passing through the coil of a pre-heater, before injection into the glycerin, which itself has been previously heated by means of a closed steam-coil. The superheating coil is heated by boiler steam. The working of the *Van Ruymbeke* still, which is employed extensively both in England and on the Continent, and is capable of yielding a very high grade glycerin, is described in detail by Webb,

'Modern Soap and Glycerine Manufacture,' London, 1927. Hot-water or air-cooled jacketed condensers are employed for the first fractions, and water-cooled condensers for the least condensable "sweet waters."

The condensates from the last few air condensers require to be concentrated subsequently by evaporation to bring them to the requisite strength. Similarly, the last condensed "sweet waters" may be concentrated, if they contain sufficient glycerin to justify the treatment.

Similar principles are involved in the *Scott*, and the *Blair, Campbell and McLean* processes.

Considerable economy in steam consumption is effected by the so-called "closed systems," favoured in the United States. In the American *Wood* plant the stills are arranged in series; the vapours from the first still are only cooled to such an extent that the strongest glycerin liquors are condensed, whilst the steam passes on through the next unit, and so on, until, at the end of the series, the vapours are taken through a water-cooled condenser to the sweet-water collector.

The steam obtained from the evaporation of the very dilute glycerin distillates ("sweet waters") is used as the heating fluid for the evaporator, which in turn supplies the steam to be injected into the glycerin still (*cf. also the Wurster-Sanger and Garrigue* systems, which are described fully by J. W. Lawrie, "Glycerol and the Glycols," London and New York, 1928).

The economy of this system is offset by the inherent disadvantage, that volatile impurities present in the sweet-water condensate are returned to the evaporator, and so recirculated throughout the whole system. The quality of the glycerin obtained by this method is no better, and may be lower, than that prepared by the *Van Ruymbeke* process.

One distillation of crude glycerin, especially in the case of soap-lye glycerin, may not give a satisfactory product for nitrating purposes, owing to contamination with sodium chloride and organic impurities (volatile fatty acids and even polyglycerols), and a second distillation becomes imperative.

The yield obtainable from crude glycerin depends, just like the distillation itself, on the care of the operator. The losses incurred by faulty methods are large, and may range from as much as 15 to even 40%. A large proportion of the loss is due to destruction of glycerol with the formation of volatile acids and acrolein on the one hand, and to the formation of polyglycerols on the other. The polyglycerols which are formed in the course of distillation should remain in the still itself, and are found with the still residue (*see below*).

The distilled glycerin liquors collected from the columns are treated with char, if required, to remove some organic impurities, and, at the same time, to clarify the glycerin and improve its colour. The collected and filtered glycerin liquors are finally concentrated in a vacuum evaporator, up to the desired specific gravity.

The commercial "distilled glycerins" vary in colour from yellow to white; they also vary in their content of glycerol according to their specific gravities, which range, as a rule, between

1.220 and 1.260. Glycerin, purified by distillation, should contain only a very small amount of ash and is thereby easily distinguished from crude glycerins.

For the grade known as dynamite glycerin, the specific gravity must be at least 1.261 at 15°. Other commercial qualities of distilled glycerin need only be concentrated to a sp.gr. of 1.250 or 1.240.

The *distilled glycerins* described above contain, as a rule, amounts of impurities, which although small, are yet sufficiently large to prohibit their employment for pharmaceutical and dietetic purposes. The "distilled glycerins" must therefore be subjected to a second distillation. If this distillation be carried out with sufficient care, the distillates give, after concentration and treatment with char, the *chemically pure (C.P.) glycerin* of commerce.

At a time when the art of preparing chemically pure glycerin was not so far advanced as it is at present, some chemically pure glycerin was manufactured by allowing glycerin to crystallise, and centrifuging the crystals, whereby the impurities were removed with that portion of glycerin which melted in the centrifugal machine. This process has, however, been abandoned, not only on account of its costliness, but also on account of the inferiority of the product as compared with the best brands of chemically pure glycerin obtained by careful distillation, since it was found that the crystals were apt to occlude impurities.

As stated above, C.P. glycerin for edible purposes must be virtually free from arsenic (*cf. below*). Such glycerin is most conveniently prepared by the distillation of arsenic-free crudes. A. C. Langmuir (*Ind. Eng. Chem.* 1932, **24**, 378) states, however, that arsenic compounds may be effectively removed from 20–25% distilled glycerin by agitating the hot glycerin with powdered cast-iron borings by means of an air-jet. In the case of more concentrated distilled glycerin, this may be freed from arsenic by treating it with 0.05–0.1% (calc. on the anhyd. glycerol present) of potassium permanganate which has been previously dissolved in sufficient water<sup>1</sup> to reduce the concentration of the glycerin to 65%; the mixture is heated to 90–5°C., made alkaline with 0.3% caustic soda and filter-pressed. The excess of

<sup>1</sup> *Warning*: If concentrated glycerol comes into contact with *dry* potassium permanganate, even in the cold, the mixture ignites spontaneously with the production of an intensely hot flame and red hot residue (Langmuir, *l.c.*; see p. 56).

alkali serves to hold back volatile fatty acids during the subsequent distillation.

Electro-osmotic processes of decolorising and purifying glycerin have been patented (B.P. 144727, 145046, 146865, of 1920).

Chemically pure glycerin is obtainable in commerce in the following "strengths": sp.gr 1.24, 1.25 and 1.26. That of the highest specific gravity approaches, as nearly as is possible for a product made on a large scale, the chemical substance glycerol.

Glycerol (pure glycerin) is a hygroscopic, odourless, colourless, highly viscid liquid, having a sweet taste. The preparation demanded by the Pharmacopœias of different countries is the purest commercial article, which consists practically of glycerol containing a very small amount of water. Glycerol is optically inactive, and is neutral to litmus. On exposure to intense cold for a prolonged time it crystallises in rhombic bisphenoid forms (*see* Lang, Poggen-dorff's *Ann. Phys. Chem.* 1874, **152**, 637; *cf.* Henninger, *Bull. Soc. chim.* 1875, [ii], **23**, 434). By seeding with a few crystals, large quantities of glycerol can easily be solidified at a temperature even above the freezing-point of water. The freezing-points of aqueous glycerol solution are shown in Table XV (p. 64).

The crystals have m.p. 18°C. (Sampsoen, *Compt. rend.* 1926, **182**, 846; *cf.* Gibson and Giauque, *J. Amer. Chem. Soc.* 1923, **45**, 93; confirmed by Pushin and Glagoleva, *J.C.S.* 1922, **121**, 2818). The latter authors find glycerol to have a cryoscopic constant of approximately 3.1.

Glycerol is oily to the touch, and produces on the skin, especially on the mucous membrane, the sensation of heat, owing to its absorbing moisture from the tissues. The water-absorbing power of glycerol is so great that, on exposure to the atmosphere, it takes up as much as 50% of its weight of water.

The determination of the *specific gravity* of pure glycerol has been attempted by many workers (Kailan, Gerlach, Skalweit, Lenz, Strohmer and others), whose results show considerable disagreement, which is due, no doubt, to the difficulty of removing the last traces of water. The values of 1.26414 at 15°/4° found by Kailan (*Z. anal. Chem.* 1912, **51**, 81) and 1.26533 at 15.5°/15.5° by A. C. Langmuir (*Ind. Eng. Chem.* 1921, **13**, 944), are in good agreement with those recorded by other chemists and with the figures published by Bosart and Snoddy (*ibid.* 1927, **19**, 506; 1928, **20**, 1377) and reproduced below (Table II).

TABLE II.—SPECIFIC GRAVITY AND DENSITY OF PURE GLYCEROL (Bosart and Snoddy).

Specific gravity at . . .	15°/15°.	15.5°/15.5°	20°/20°.	25°/25°.
Apparent sp.gr. (in air) . . .	1.26557	1.26532	1.26362	1.26201
True sp.gr. (weighings reduced to vacuum) . . .	1.26526	1.26501	1.26331	1.26170
Absolute density <sup>1</sup> . . .	1.26415/15° 0	1.26381/15.5°	1.26108/20°	1.25802/25°

<sup>1</sup> *I.e.* = sp.gr. related to water at maximum density, all weighings being reduced to vacuum.



Values for the specific gravity of aqueous glycerol solutions at 15°/15° and 20°/20° determined by Bosart and Snoddy are shown in Table III: full tables showing apparent sp.gr. at 15.5°/15.5° and 25°/25°, true specific gravities (*in vacuo*), absolute densities and coefficients of expansion of glycerol solutions are given in the original papers.

The figures of Bosart and Snoddy were obtained as the result of a most careful and exhaustive investigation, and must be regarded as the most trustworthy data at present available. They agree closely with results obtained in the Eastern Laboratory of the E. I. Du Pont de Nemours Co. from which Table IV has been constructed.

TABLE III.—SPECIFIC GRAVITY OF GLYCEROL SOLUTIONS (Bosart and Snoddy).

Glycerol % by weight.	Apparent specific	$\gamma$ <sup>1</sup> (in air).	Glycerol % by weight.	Apparent specific gravity <sup>1</sup> (in air).
	15°/15°	20°/20°		15°/15° 20°/20°
100	1.26557	1.26362	50	1.12985 1.12845
99	1.26300	1.26105	49	1.12710 1.12570
98	1.26045	1.25845	48	1.12440 1.12300
97	1.25785	1.25585	47	1.12165 1.12030
96	1.25525	1.25330	46	1.11890 1.11760
95	1.25270	1.25075	45	1.11620 1.11490
94	1.25005	1.24810	44	1.11345 1.11220
93	1.24740	1.24545	43	1.11075 1.10950
92	1.24475	1.24280	42	1.10800 1.10680
91	1.24210	1.24020	41	1.10525 1.10410
90	1.23950	1.23755	40	1.10255 1.10135
89	1.23680	1.23490	39	1.09985 1.09870
88	1.23415	1.23220	38	1.09715 1.09605
87	1.23150	1.22955	37	1.09445 1.09335
86	1.22885	1.22690	36	1.09175 1.09070
85	1.22620	1.22420	35	1.08905 1.08805
84	1.22355	1.22155	34	1.08635 1.08535
83	1.22090	1.21890	33	1.08365 1.08270
82	1.21820	1.21620	32	1.08100 1.08005
81	1.21555	1.21355	31	1.07830 1.07735
80	1.21290	1.21090	30	1.07560 1.07470
79	1.21015	1.20815	29	1.07295 1.07210
78	1.20740	1.20540	28	1.07035 1.06950
77	1.20465	1.20270	27	1.06770 1.06690
76	1.20190	1.19995	26	1.06510 1.06435
75	1.19915	1.19720	25	1.06250 1.06175
74	1.19640	1.19450	24	1.05985 1.05915
73	1.19365	1.19175	23	1.05725 1.05655
72	1.19090	1.18900	22	1.05460 1.05400
71	1.18815	1.18630	21	1.05200 1.05140
70	1.18540	1.18355	20	1.04935 1.04880
69	1.18260	1.18080	19	1.04685 1.04630
68	1.17985	1.17805	18	1.04435 1.04380
67	1.17705	1.17530	17	1.04180 1.04135
66	1.17430	1.17255	16	1.03930 1.03885
65	1.17155	1.16980	15	1.03675 1.03635
64	1.16875	1.16705	14	1.03425 1.03390
63	1.16600	1.16430	13	1.03175 1.03140
62	1.16320	1.16155	12	1.02920 1.02890
61	1.16045	1.15875	11	1.02670 1.02640
60	1.15770	1.15605	10	1.02415 1.02395
59	1.15490	1.15325	9	1.02175 1.02155
58	1.15210	1.15050	8	1.01935 1.01915
57	1.14935	1.14775	7	1.01690 1.01675
56	1.14655	1.14500	6	1.01450 1.01435
55	1.14375	1.14220	5	1.01210 1.01195
54	1.14100	1.13945	4	1.00965 1.00955
53	1.13820	1.13670	3	1.00725 1.00720
52	1.13540	1.13395	2	1.00485 1.00480
51	1.13265	1.13120	1	1.00240 1.00240

Accurate to the nearest 5 in the 5th place.

TABLE IV.—*w/w* PER CENT. GLYCEROL CORRESPONDING TO SPECIFIC GRAVITY AT 15.6°/15.6° C.<sup>1</sup>

Sp. gr.	1.		2.	3.		4.	5.	6.	7.	8.
1.252	—		—	—		95.00	95.03	95.07	95.11	95.15
1.253	95.23	95.27	95.31	95.35	95.39	95.43	95.46	95.50	95.54	—
1.254	95.62	95.65	95.69	95.73	95.77	95.80	95.84	95.88	95.92	—
1.255	96.00	96.03	96.07	96.11	96.15	96.19	96.23	96.26	96.30	—
1.256	96.38	96.42	96.46	96.50	96.54	96.58	96.62	96.66	96.70	—
1.257	96.78	96.82	96.86	96.90	96.94	96.98	97.02	97.05	97.09	—
1.258	97.17	97.21	97.24	97.28	97.32	97.36	97.40	97.44	97.48	—
1.259	97.56	97.60	97.64	97.68	97.72	97.76	97.80	97.84	97.88	—
1.260	97.96	98.00	98.03	98.07	98.11	98.15	98.19	98.23	98.26	—
1.261	98.34	98.38	98.41	98.45	98.49	98.53	98.57	98.60	98.64	—
1.262	98.72	98.76	98.80	98.84	98.88	98.92	98.96	99.00	99.03	—
1.263	99.11	99.15	99.19	99.22	99.26	99.30	99.34	99.37	99.41	—
1.264	99.49	99.53	99.56	99.60	99.64	99.68	99.72	99.76	99.80	—
1.265	99.88	99.92	99.96	100.00	—	—	—	—	—	—

<sup>1</sup> Du Pont de Nemours & Co., reproduced through J. W. Lawrie, "Glycerol and the Glycols," p. 291.

The specific gravity data of Bosart and Snoddy supersede those of the earlier investigators, including Gerlach, whose tables have gained wide currency in the past; Bosart (*ibid.* 1921, 13, 944; and *l.c.*) has shown that, whilst Gerlach's sp.gr. at 15°/15° are sufficiently accurate to be usable for technical purposes, his table of values at 20°/20° must be discarded entirely.

Provided a specimen of C.P. glycerol satisfies the qualitative tests for purity described on p. 58c, the proportion of glycerol in it may be deduced from a determination of the specific gravity by the pycnometric method with the help of the tables referred to above.

The variation in the rate of expansion<sup>1</sup> of solutions of glycerol with temperature (*i.e.* the change in specific gravity with temperature) is shown in Table V (Bosart and

TABLE V.—RATE OF EXPANSION OF GLYCEROL SOLUTIONS (Bosart and Snoddy)

Glycerol, concentration %	Change in specific gravity per °C.		
	15-20°	15-25°	20-25°
100	0.000615	0.000615	0.000610
97.5	0.000620	0.000615	0.000605
95	0.000615	0.000615	0.000615
90	0.000610	0.000615	0.000620
80	0.000620	0.000615	0.000610
70	0.000580	0.000570	0.000505
60	0.000540	0.000545	0.000550
50	0.000485	0.000495	0.000510
40	0.000430	0.000435	0.000445
30	0.000370	0.000385	0.000400
20	0.000300	0.000315	0.000325
10	0.000230	0.000255	0.000280
0	0.000180	0.000205	0.000230

Snoddy, *ibid.* 1927, 19, 506; cf. Hehner, J.S.C.I. 1889, 8, 8; Gerlach, Z. anal. Chem. 1885, 24, 111; Comey and Backus, J. Ind. Eng. Chem. 1910, 2, 11); hence it is necessary, when correcting specific gravities from experimental to

<sup>1</sup> Bosart and Snoddy adopt the expression "rate of expansion" to denote the rate of change of the *specific gravity* per degree of temperature in order to avoid confusion with the true "coefficient of expansion," which applies only to the change of *volume* with temperature.

standard temperatures, to use the factor corresponding to the temperature at which the determination is made.

The following formulae have been computed by Bosart and Snoddy for the purpose of calculating the specific gravity of glycerol solutions at 15°/15° and 25°/25° when the actual determination has been made at another experimental temperature:

(i) For calculating from a higher to a lower temperature—

$$d = \frac{ab + Bc(T-t)}{c}$$

(ii) For calculating from a lower to a higher temperature—

$$a = \frac{dc - Bc(T-t)}{b}$$

where *a* = sp.gr. of glycerol at T°/T°.

*d* = " " " " t°/t°.

*b* = sp.gr. of water at T°.

*c* = " " " " t°.

*B* = change in sp.gr. of glycerol per °C.

*T* = higher temp. of sp.gr. determination.

*t* = lower " " "

Analogous formulae and tables are given by Comey and Backus (*l.c.*). For dynamite glycerins, round figures for the values of the average rates of expansion, viz. 0.00061, 0.000615 and 0.00062 at 20°, 25° and 30° respectively, are convenient to remember and sufficiently accurate for most practical purposes.

In cases when the volume of the available sample does not permit of accurate determination of specific gravity, the content of glycerol may be derived from the *refractive index* of the specimen. The Abbé refractometer is convenient and rapid in use and only requires a few drops of material, but the reading is of somewhat doubtful accuracy in the fourth place of decimals so that refractive indices determined with this instrument must be regarded as a less accurate indication of the concentration of glycerol solutions than determinations of specific gravity (Hoyt). More accurate results (permitting the determination of concentration to within 0.1%) can be obtained by the use of the

TABLE VI.—REFRACTIVE INDEX OF GLYCEROL SOLUTIONS AT 15°C. (Skalweit) AND 20°±0.5° (Hoyt).

Glycerol weight.	Sp. gr. at 15° com- pared with water at 15° (Skalweit).	Refractive index at 15° (Skalweit).	Refractive index at 20° (Hoyt).	Glycerol weight.	Sp. gr. at 15° com- pared with water at 15° (Skalweit).	Refractive index at 15° (Skalweit).	Refractive index at 20° (Hoyt).
0	1.0000	1.3330	1.33303	51	1.1318	1.4010	1.43958
1	1.0024	1.3342	1.33416	52	1.1346	1.4024	1.40107
2	1.0048	1.3354	1.33530	53	1.1374	1.4039	1.40256
3	1.0072	1.3366	1.33645	54	1.1402	1.4054	1.40405
4	1.0096	1.3378	1.33762	55	1.1430	1.4069	1.40554
5	1.0120	1.3390	1.33880				
6	1.0144	1.3402	1.33909	56	1.1458	1.4084	1.40703
7	1.0168	1.3414	1.34118	57	1.1486	1.4099	1.40852
8	1.0192	1.3426	1.34238	58	1.1514	1.4104	1.41001
9	1.0216	1.3439	1.34359	59	1.1542	1.4129	1.41150
10	1.0240	1.3452	1.34481	60	1.1570	1.4144	1.41299
				61	1.1599	1.4160	1.41448
11	1.0265	1.3464	1.34604	62	1.1628	1.4175	1.41597
12	1.0290	1.3477	1.34729	63	1.1657	1.4190	1.41746
13	1.0315	1.3490	1.34834	64	1.1686	1.4205	1.41895
14	1.0340	1.3503	1.34980	65	1.1715	1.4220	1.42044
15	1.0365	1.3516	1.35106				
				66	1.1743	1.4235	1.42193
16	1.0390	1.3529	1.35223	67	1.1771	1.4250	1.42342
17	1.0415	1.3542	1.35361	68	1.1799	1.4265	1.42491
18	1.0440	1.3555	1.35490	69	1.1827	1.4280	1.42640
19	1.0465	1.3568	1.35619	70	1.1855	1.4295	1.42789
20	1.0490	1.3581	1.35740				
				71	1.1882	1.4309	1.42938
21	1.0516	1.3594	1.35879	72	1.1909	1.4324	1.43087
22	1.0542	1.3607	1.36010	73	1.1936	1.4339	1.43236
23	1.0568	1.3620	1.36141	74	1.1963	1.4354	1.43385
24	1.0594	1.3633	1.36272	75	1.1990	1.4369	1.43534
25	1.0620	1.3647	1.36404				
				76	1.2017	1.4384	1.43683
26	1.0646	1.3660	1.36536	77	1.2044	1.4399	1.43832
27	1.0672	1.3674	1.36669	78	1.2071	1.4414	1.43982
28	1.0698	1.3687	1.36802	79	1.2098	1.4429	1.44135
29	1.0724	1.3701	1.36936	80	1.2125	1.4444	1.44290
30	1.0750	1.3715	1.37070				
				81	1.2152	1.4460	1.44445
31	1.0777	1.3729	1.37204	82	1.2179	1.4475	1.44612
32	1.0804	1.3743	1.37338	83	1.2206	1.4490	1.44770
33	1.0831	1.3757	1.37472	84	1.2233	1.4505	1.44930
34	1.0858	1.3771	1.37606	85	1.2260	1.4520	1.45085
35	1.0885	1.3785	1.37740				
				86	1.2287	1.4535	1.45237
36	1.0912	1.3799	1.37874	87	1.2314	1.4550	1.45389
37	1.0939	1.3813	1.38008	88	1.2341	1.4565	1.45539
38	1.0966	1.3827	1.38143	89	1.2368	1.4580	1.45689
39	1.0993	1.3840	1.38278	90	1.2395	1.4595	1.45839
40	1.1020	1.3854	1.38413				
				91	1.2421	1.4610	1.45989
41	1.1047	1.3868	1.38548	92	1.2447	1.4625	1.46139
42	1.1074	1.3882	1.38683	93	1.2473	1.4640	1.46290
43	1.1101	1.3896	1.38818	94	1.2499	1.4655	1.46443
44	1.1128	1.3910	1.38953	95	1.2525	1.4670	1.46597
45	1.1155	1.3924	1.39089				
				96	1.2550	1.4684	1.46752
46	1.1182	1.3938	1.39227	97	1.2575	1.4698	1.46909
47	1.1209	1.3952	1.39368	98	1.2600	1.4712	1.47071
48	1.1236	1.3966	1.39513	99	1.2625	1.4728	1.47234
49	1.1263	1.3981	1.39660	100	1.2650	1.4742	1.47399
50	1.1290	1.3996	1.39809				

dipping or immersion refractometer. The original Zeiss instrument did not allow of testing more concentrated solutions than those containing 26% of glycerol,<sup>1</sup> but improved modern types with interchangeable prisms, such as that used by Hoyt for the determinations reproduced below, enable accurate measurements to be made over the whole range of solutions from 0 to 100% glycerol.

The figures for refractive indices at 20°C. shown in Table VI have been computed by Hoyt (Ind. Eng. Chem. 1934, **26**, 329) from the results of the examination, by means of such an immersion refractometer, of 30 samples of diluted glycerin solutions prepared from a highly

purified specimen of double-distilled C.P. glycerin. There have been included in the same table values for the refractive indices and specific gravities of glycerol solutions at 15°C., published by Skälweit (Rep. anal. Chem. 1885, **5**, 17); this author used an Abbé refractometer, the experimental observations being made on "numerous diluted samples" prepared from crystallised glycerol. Wagner's table of refractive indices of dilute glycerol solutions (*w/v*%) at 17.5°C. determined by means of a Zeiss immersion refractometer is shown in Table VII (from Wagner, "Immersion Refractometer Tables," 1907, p. 46, Table 70; reproduced through Hoyt, Oil and Soap, 1933, **10**, 43).

TABLE VII.—REFRACTIVE INDEX OF DILUTE GLYCEROL SOLUTIONS (*w/v*%) AT 17.5°C. (Wagner).

Scale reading, Zeiss.	Refractive index.	<i>w/v</i> % glycerol, g per 100 c.c.	Scale reading, Zeiss.	Refractive index.	<i>w/v</i> % glycerol, g per 100 c.c.	Scale reading, Zeiss.	Refractive index.	<i>w/v</i> % glycerol, g per 100 c.c.
15	1.33320	0.00	46	1.34650	10.01	76	1.35750	19.48
16		0.33	47		10.33	77		19.79
17		0.66	48		10.65	78		20.10
18		0.99	49		10.96	79		20.41
19		1.32	50		11.28	80		20.72
20	1.33513	1.64	51	1.34836	11.59	81	1.35930	21.03
21		1.97	52		11.91	82		21.34
22		2.29	53		12.22	83		21.65
23		2.62	54		12.54	84		21.96
24		2.94	55		12.86	85		22.27
25	1.33705	3.27	56	1.35021	13.17	86	1.36109	22.58
26		3.59	57		13.49	87		22.89
27		3.92	58		13.81	88		23.20
28		4.24	59		14.12	89		23.50
29		4.56	60		14.44	90		23.81
30	1.33896	4.88	61	1.35205	14.75	91	1.36287	24.12
31		5.21	62		15.07	92		24.43
32		5.53	63		15.38	93		24.73
33		5.85	64		15.70	94		25.04
34		6.17	65		16.02	95		25.35
35	1.34086	6.49	66	1.35388	16.33	96	1.36464	25.66
36		6.81	67		16.65	97		25.96
37		7.13	68		16.96	98		26.26
38		7.45	69		17.28	99		26.57
39		7.77	70		17.59	100		26.88
40	1.34275	8.09	71	1.35569	17.91	101	1.36640	27.18
41		8.41	72		18.22	102		27.49
42		8.73	73		18.54	103		27.80
43		9.05	74		18.85	104		28.11
44		9.37	75		19.16	105		28.41
45	1.34463	9.69				106		28.72

Table VIII, due to Hoyt (*loc. cit.* 1934), shows the refractive index of pure glycerol at various temperatures.

The figures given imply a temperature coefficient for the refractive index of 99.84% glycerol averaging  $-0.000225$  per 1°C. over the range 10–20°C. This is somewhat lower than the figures of  $0.00028/1^\circ\text{C.}$  and  $0.00026/1^\circ\text{C.}$

<sup>1</sup> It is not permissible to dilute concentrated glycerin with a known amount of water to a lower percentage, and then to determine the refractive index, inasmuch as contraction takes place on mixing glycerin with water (*see* p. 536).

over the range 12.5–17.5°C. reported by Wolff (Z. angew. Chem. 1919, **32**, I, 148) for glycerol of 86% and 77% concentration respectively<sup>2</sup>: Van der Willigen (Fortschr. d. Physik, 1869, **25**, 288) gives temperature coefficients of refractive index varying from  $-0.00021/1^\circ\text{C.}$  for glycerol of approx. 45% concentration to  $-0.00025/1^\circ\text{C.}$  for a 90% (approx.) glycerin. Listing (*ibid.* 1869, **25**, 294) reported a change in refractive

<sup>2</sup> The concentrations mentioned here and in the next few lines are computed from the specific gravity data given by the original authors, with the aid of the Bosart-Snoddy tables.

TABLE VIII.—REFRACTIVE INDEX OF PURE GLYCEROL (99.84%) AT VARIOUS TEMPERATURES (Hoyt).

Temp., °C.	Refractive index, " <i>n</i> <sub>D</sub> "
10.2 . . . . .	1.47592
11.2 . . . . .	1.47575
12.2 . . . . .	1.47552
12.8 . . . . .	1.47536
13.8 . . . . .	1.47512
15.0 . . . . .	1.47485
15.8 . . . . .	1.47464
17.6 . . . . .	1.47418
18.0 . . . . .	1.47408
20.0 . . . . .	1.47367

index of  $-0.00032$  per °C. for glycerol of about 96% concentration. The temperature coefficient of the refractive index of glycerol solutions is obviously a function of concentration and hence would be expected to become numerically smaller as the dilution increases, since the average temperature coefficient of refractive index of pure water is  $-0.000081$  per 1°C. over the range 10–20°C.

Glycerol boils at 290° (corr.) under 760 mm. (759.7 mm. corr.) pressure (Mendeléef, *Annalen*, 1860, 114, 167; cf. Gerlach, *Z. anal. Chem.* 1885, 24, 110) with only slight decomposition; it distils unchanged under considerably reduced pressure, and table IX contains the most trustworthy observations of the b.p. of glycerol under reduced pressures (cf. also Richardson, *J.C.S.* 1886, 49, 746; Kailan, *Z. anal. Chem.* 1912, 51, 81):

TABLE IX.

Pressure, mm	Boiling-point °C.
385.33	260.4
347.10	257.3
231.87	250.3
201.23	241.8
100.81	220.3
50.00	210.0
45.61	201.3
30.00	191.8
20.46	183.3
12.50	179.5
10.00	167.2
6.53	161.3
5.00	155.5
0.24	118.5
0.056	115–116

Glycerol is miscible with water in all proportions. The mixing is accompanied by a contraction of volume and an increase of temperature. The greatest increase of temperature, viz. 5°, is observed when 58 parts of glycerol (by weight) are mixed with 42 parts of water; the greatest contraction is 1.1% (Gerlach). Glycerin can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid for a prolonged period.

Glycerol does not volatilise at the ordinary temperature, but from concentrated solutions appreciable quantities volatilise with water vapour at 100°.

The vapour pressure of a dilute solution of glycerol falls as its normal boiling point increases. Since glycerol and water are miscible in every proportion, the composition of the escaping vapours cannot be calculated according to Dalton's law, but must be derived from actual observations. Gerlach determined, by a barometric method, the vapour pressures given in Table X.

TABLE X.—VAPOUR PRESSURES OF GLYCEROL AND OF AQUEOUS SOLUTIONS OF GLYCEROL (Gerlach).

Glycerol %.	Water %.	B.p. at 760 mm. pressure, °C.	Vapour pressure at 100 °C mm. of mercury.
100	0	290	64
99	1	239	87
98	2	208	107
97	3	188	126
96	4	175	144
95	5	164	162
94	6	156	180
93	7	150	198
92	8	145	215
91	9	141	231
90	10	138	247
89	11	135	263
88	12	132.5	279
87	13	130.5	295
86	14	129	311
85	15	127.5	326
84	16	126	340
83	17	124.5	355
82	18	123	370
81	19	122	384
80	20	121	396
79	21	120	408
78	22	119	419
77	23	118.2	430
76	24	117.4	440
75	25	116.7	450
74	26	116	460
73	27	115.4	470
72	28	114.8	480
71	29	114.2	489
70	30	113.6	496
65	35	111.3	553
60	40	109	565
55	45	107.5	593
50	50	106	618
45	55	105	639
40	60	104	657
35	65	103.4	675
30	70	102.8	690
25	75	102.3	704
20	80	101.8	717
10	90	100.9	740
0	100	100	760

Up to a concentration of about 50%, no glycerol escapes with the water vapours, even if the dilute solutions be kept boiling for a prolonged time. At a concentration of about 70%, traces of glycerol escape from the boiling solution (Hehner, *Analyst*, 1887, 12, 65). The

## GLYCERIN.

TABLE XI.—ABSOLUTE VISCOSITIES (CENTIPOISES) OF GLYCEROL SOLUTIONS (Sheely).  
(Experimental data : Interpolated values for every 10% glycerol shown in black type.)

Per cent Glycerol.	Viscosity (centipoises) at				
	20°C.	22.5°C.	25°C.	27.5°C.	30°C.
0.0 (water)	1 005		0.893	—	0.800
3.85	1.109	—	0.981	—	0.877
7.31	1.216	—	1.073	—	0.956
10.0	1 311	—	1.153	—	1.024
10.58	1 331	—	1.172	—	1.040
14.13	1 478	—	1.295	—	1.147
17.40	1 634	—	1.428	—	1.259
19.79	1.756	—	1.530	—	1.351
20.0	1.769	—	1.542	—	1.360
23.55	1.995	—	1.731	—	1.520
27.98	2 323	—	2.007	—	1.751
30.00	2.501	—	2.157	—	1.876
30.44	2.545	—	2.191	—	1.907
33.11	2 822	—	2.420	—	2.098
36.29	3 207	—	2.741	—	2.364
39.02	3.595	—	3 054	—	2.625
40.0	3.750	—	3 181	—	2.731
41.60	4.029	—	3.407	—	2.919
44.78	4.668	—	3.927	—	3.347
48.20	5 518	—	4.611	—	3.909
50.0	6 050	—	5 041	—	4.247
51.33	6 516	—	5.409	—	4.552
54.10	7.600	—	6.266	—	5.236
55.59	8.282	7.494	6.804	6.203	5.679
57.12	9.092	8.209	7.447	6.776	6.187
58.74	10 070	9 074	8.184	7.430	6.770
59.74	10 787	9 679	8.756	7.918	7.222
60.0	10.96	9.83	8.823	8.015	7.312
61.46	12 061	10.793	9.731	8.792	7.986
62.50	—	11.642	10.473	9.438	8.548
64.50	14.99	13.35	11.96	10.79	9.750
64.66	15.13	13.46	12.05	10.84	9.80
66.94	17.89	15.86	14.12	12.68	11.40
70.0	22.94	20.23	17.96	15.96	14.32
70.19	23.35	20.53	18.21	16.23	14.53
72.40	28.57	24.98	22.03	19.56	17.41
74.61	35.11	30.57	26.81	23.64	20.97
75.69	38.98	33.80	29.61	26.06	23.02
77.71	47.97	41.41	36.08	31.58	27.81
79.37	57.79	49.52	42.85	37.49	32.86
80.0	62.0	52.77	45.86	40.00	34.92
80.83	70.28	60.08	51.90	—	—
82.80	85.73	72.75	62.53	54.01	46.90
84.27	103.17	87.23	74.50	64.08	55.29
86.07	131.08	110.20	93.52	79.81	68.64
86.56	140.42	117.87	99.86	85.20	73.12
87.89	172.2	143.4	120.9	102.7	87.65
89.89	231.6	191.5	160.6	135.1	114.5
90.0	234.6	194.6	163.6	137.3	115.3
90.81	268.0	220.5	183.8	154.4	130.4
92.19	337.9	276.5	229.2	191.6	161.0
92.82	375.6	306.8	254.7	212.1	177.9
93.70	442.3	359.9	295.9	245.6	205.9
94.32	481.7	390.7	321.5	266.3	222.3
95.0	545.0	443.8	366.0	301.8	248.8
95.19	565.6	457.6	374.9	309.7	257.2
95.65	618.5	499.5	408.3	336.6	279.6
96.08	671.6	542.1	441.8	363.6	300.6
96.48	724.0	582.9	474.8	380.9	322.4
96.89	783.5	629.6	512.3	420.7	346.7
98.06	986.0	789.9	636.8	519.8	427.2
98.84	1158	926.0	747.0	607.3	496.2
99.66	1385	1102	884.0	715.5	583.3
100.0	1499	1186	945.0	764.0	624.0

boiling-point of such a solution is 113.6° (see table). Above this concentration, noticeable amounts of glycerol escape, so that the quantitative determination of glycerol in an aqueous solution by evaporating it down on the water-bath leads to faulty results. Even if the concentration of glycerol solutions be carried out *in vacuo*, considerable proportions of glycerol escape with the water vapour when the concentration of the solution exceeds 80% (Lewkowitsch).

On heating glycerol slowly in a platinum dish to 150–160°, it evaporates gradually without leaving a residue; at 150° it will burn with a bluish non-luminous flame without emitting any odour. If, however, glycerol is heated rapidly in a platinum dish, it burns with formation of acrolein, and yields a residue consisting of polyglycerols.

*Viscosity of Aqueous Glycerol Solutions.*—The most accurate figures for the viscosities of

aqueous glycerol solutions appear to be those of Sheely, whose experimental values are reproduced in Table XI (a full table, prepared by interpolation, is given in the original memoir, *Ind. Eng. Chem.* 1932, **24**, 1060). The concentrations of the test-solutions were deduced from the observed specific gravities (not quoted) by the help of the Bosart and Snoddy tables. The viscosities found agree fairly closely with the few experimental values of Archbutt and Deeley ("Lubrication and Lubricants," 5th ed., London, 1927, p. 196), but diverge appreciably from figures given by Herz and Wegner (*Z. deut. Oel- u. Fett-Ind.* 1925, **45**, 401), particularly for the higher concentrations, at which the discrepancy may amount to 5–10%. Although the accuracy of the Herz and Wegner figures is under question, it has been thought advisable to reproduce their table of relative viscosities (see Table XII) since this covers a wide range of temperatures, for which no other figures are

TABLE XII.—RELATIVE VISCOSITIES OF AQUEOUS GLYCEROL SOLUTIONS AS COMPARED WITH WATER. (Herz and Wegner, Darke and Lewis.)

Wt. % Glycerol.		Temperature °C.									
Herz and Wegner.	Corrected values, Sheely. <sup>1</sup>	1°	10°	15°	20°	30°	40°	50°	60°	70°	80°
10	0.77	1.366	1.344	1.331	1.321	1.275	1.274	1.272	1.216	1.212	1.189
20	10.06	1.902	1.876	1.857	1.834	1.753	1.636	1.508	1.518	1.462	1.445
30	29.66	2.613	2.603	2.558	2.503	2.358	2.210	2.086	1.094	1.875	1.835
40	39.83	4.329	4.175	4.023	3.858	3.516	3.198	2.958	2.620	2.495	2.342
50	50.12	7.105	6.775	6.256	5.892	5.190	4.621	4.100	3.835	3.166	3.359
60	59.94	13.150	12.27	11.20	10.26	8.807	7.568	6.712	5.004	5.359	5.084
70	69.98	34.230	30.82	26.90	24.11	18.42	14.19	12.14	10.11	8.732	7.801
80	79.85	100.580	88.46	74.23	63.31	43.67	30.75	24.30	19.41	15.96	11.46
85	84.81	190.4	151.4	144.2	99.05	66.84	47.97	35.36	27.00	21.06	17.52
88	87.62	274.6	230.5	181.3	147.8	99.63	68.10	44.77	35.50	26.48	21.32
90	89.30	419.4	324.9	254.3	194.3	123.5	86.46	61.60	43.81	32.08	25.25
92	91.69	—	473.3	374.1	283.0	186.4	110.4	77.24	56.50	39.42	30.64
Water viscosity in centipoises <sup>3</sup>		—	1.3061	1.1406	1.0046	0.8019	0.6533	0.5497	0.4701	0.4062	0.3556

<sup>1</sup> Glycerol concentrations re-calculated from the data of Herz and Wegner by Sheely, using the specific gravity concentration tables of Bosart and Snoddy.

The first column gives the concentration derived by

<sup>2</sup> Darke and Lewis, *Chem. and Ind.* 1928, **6**, 1078.

<sup>3</sup> Landolt-Börnstein, 5th ed., 1st Suppl., 1927, p. 83 (after Bingham and Jackson, 1917).

available. Some supplementary figures, due to Darke and Lewis (*Chem. and Ind.* 1928, **6**, 1078), have been included. Herz and Wegner used the less accurate specific-gravity tables compiled by themselves to ascertain the concentrations of their test solutions. For purposes of comparison, therefore, Sheely has applied the Bosart and Snoddy tables to recalculate the concentrations in question from the data supplied by the earlier authors; these corrected values have been inserted in Table XII.

Figures for absolute viscosities calculated from the experimental data of Table XII are given in the original paper by Herz and Wegner,<sup>1</sup> (*cf. also* Cocks, *J.S.C.I.* 1929, **48**, 279r).

Glycerol is miscible with alcohol in all pro-

<sup>1</sup> The values for the viscosity of water used for calculation by Herz and Wegner were taken from the 5th ed. (1923) of the tables of Landolt-Börnstein and are not quite identical with the revised values (due to Bingham and Jackson) given in the 1st Suppl. (1927) of Landolt-Börnstein.

portions, dissolves readily in a mixture of alcohol and ether, but is sparingly soluble in ether alone (1 part of glycerol, sp-gr. 1.23, requiring about 500 parts of ether) it is therefore impossible to extract glycerol from its aqueous solution by means of ether. Glycerol is soluble in acetone. Nine parts of glycerol dissolve in 100 parts of ethyl acetate. It is insoluble in chloroform, light petroleum, carbon disulphide or benzene; it is also insoluble in oils and fats (Lewkowitsch).

Glycerol has powerful solvent properties; it combines in this respect the properties of water and of ordinary alcohol; many substances dissolve more readily in it than in either of these two other liquids. The following list of solubilities illustrates this (Klever, *Chem. Zentr.* 1872, 434):

100 parts of glycerol dissolve at 15° 98 parts of sodium carbonate; 60 parts of borax; 50.5 parts of potassium arsenate; 50 parts of sodium arsenate; 50 parts of zinc chloride; 48.8 parts

of tannic acid; 40 parts of alum; 40 parts of zinc iodide; 40 parts of potassium iodide; 35- $\frac{1}{2}$  parts of zinc sulphate; 32 parts of potassium cyanide; 30 parts of copper sulphate; 25 parts of ferrous sulphate; 25 parts of potassium bromide; 20 parts of lead acetate; 20 parts of ammonium carbonate; 20 parts of arsenious oxide; 20 parts of arsenic oxide; 20 parts of ammonium chloride; 15 parts of oxalic acid; 11 parts of boric acid; 10 parts of barium chloride; 10 parts of copper acetate; 10 parts of benzoic acid; 8 parts of sodium bicarbonate; 7.5 parts of mercuric chloride; 5 parts of calcium sulphide; 3.7 parts of potassium chloride; 3.5 parts of potassium chlorate; 1.9 parts of iodine; about 1 part of calcium sulphate; 0.1 part of sulphur; 0.25 part of phosphorus.

An aqueous glycerol solution, of sp.gr. 1.114, dissolves 0.057% of calcium sulphate. Metallic soaps (which are insoluble in water) are to some extent dissolved by aqueous glycerol; thus: 100 parts of glycerol solution, sp.gr. 1.114, dissolve 0.71 part of iron oleate, 0.94 part of magnesium oleate, and 1.18 parts of calcium oleate.

Glycerol is completely oxidised to carbon dioxide and water by potassium dichromate in an acid solution, and this reaction forms the basis of one of the standard methods for the quantitative determination of glycerol (*see* p. 61c). In dilute aqueous solution and in the presence of caustic alkali, potassium permanganate oxidises glycerol quantitatively to oxalic acid, carbon dioxide and water (Wanklyn and Fox, *Chem. News*, 1880, **53**, 15; Benedikt and Zsigmondy, *Chem.-Ztg.*, 1885, **9**, 975).

Dry potassium permanganate reacts violently with concentrated glycerol. If finely powdered potassium permanganate be heaped up to form a small truncated cone and concentrated glycerol be poured into a hole made in the top, fumes escape; after a very short time the glycerol commences to froth and ignites spontaneously with violent evolution of gases.

Glycerol treated with hydrogen peroxide in presence of a ferrous salt yields glyceraldehyde,  $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO}$ .

Of the eleven possible products of moderate oxidation of glycerol, ten have been isolated, viz. glyceraldehyde (glycerose), glyceric acid, dihydroxyacetone, hydroxypyrracemic acid, tartronmonoaldehyde, tartrondialdehyde, tartronic acid, mesoxalmonoaldehyde, mesoxal-dialdehyde and mesoxalic acid; hydroxypyrracemaldehyde is unknown. The glyceric acid obtained by gentle oxidation with nitric acid is a racemic compound and has been resolved into optically active enantiomorphous acids by J. Lewkowitsch (*Ber.* 1883, **16**, 2720). Further oxidation yields carbon dioxide, formic acid and water.

A strong aqueous solution of glycerol reduces Barreswill's (Fehling's) solution only slightly. If, however, the glycerol be diluted previously with 10 times its bulk of water, no reduction occurs.

A mixture of glycerol and silver nitrate solution heated at the temperature of boiling water with a few drops of ammonia, gives a precipitate of metallic silver. If ammonia

solution be added to glycerol in the cold, and heat be then applied, as a rule no reduction takes place on adding silver nitrate; the addition of caustic soda or potash, however, causes metallic silver to separate slowly.

Glycerol dissolves caustic alkalis, alkaline earths and lead oxide, forming chemical compounds (*cf.* Bullnheimer, *Ber.* 1898, **31**, 1453; 1899, **32**, 2347; 1900, **33**, 817). The compounds so formed are termed metallic *glyceroxides* or *glycerates* and are thought to have a cyclic structure resembling that of the saccharates. Lime, strontia and baryta are precipitated nearly completely from such solutions by carbon dioxide, a small quantity only of the bases escaping precipitation. In the presence of caustic alkalis, glycerol also dissolves ferric oxide, cupric oxide and bismuth oxide, no doubt in consequence of the formation of soluble compounds (metallic glyceroxides), such as are represented by monosodiumcupriglyceroxide ( $\text{NaCuC}_3\text{H}_5\text{O}_3$ ) $_2$ ·3H $_2$ O. The oxides enumerated above are not reduced to metals, or at most only to their lower oxides. The following oxides: silver oxide, gold oxide, mercury oxide, rhodium oxide, palladium oxide and platinum oxide ( $\text{Ag}_2\text{O}$ ,  $\text{Au}_2\text{O}_3$ ,  $\text{HgO}$ ,  $\text{RhO}_2$ ,  $\text{PdO}$ ,  $\text{PtO}_2$ ), are reduced to metals when heated with alkaline glycerol solution (Bullnheimer).

The great solubility of zinc sulphate, as also of nickel, cobalt and copper sulphates, in glycerol, is explained by the fact that these salts combine with 3 mol. of glycerol to form compounds (Grün and Bockisch, *ibid.* 1908, **41**, 3465) of the general formula:



Where M represents an atom of one of the above-mentioned metals. For these compounds, the name *glycerinates* has been proposed by Grün, in order to distinguish them from the metallic glyceroxides described above.

#### QUALITATIVE TESTS FOR GLYCEROL.

One of the simplest tests for glycerol, which is capable of detecting quite small quantities, is based on the penetrating odour of acrolein, which is formed when glycerol is heated in the presence of acid salts. The same odour is also noticeable when a fatty-oil lamp or tallow candle is blown out. For the test, a small portion of the substance should be heated with potassium bisulphate, and the acrolein detected either by its odour or by the red colour formed when the vapour is passed into Schiff's reagent (a solution of rosanilin which has been decolorised by sulphur dioxide). Alternatively, an ammoniacal solution of silver nitrate may be used for the detection of the acrolein which produces in it a precipitate or mirror of metallic silver.

Some other useful tests described by Denigès (*Compt. rend.* 1909, **148**, 570) are based upon the colour reactions of dihydroxyacetone which is formed when glycerol is heated with bromine water. About 0.1 g. of the glycerol is heated with 10 ml. of bromine water in a bath of boiling water for about 20 minutes or until the free bromine has disappeared. In four separate



test tubes there are placed 0.1 ml. of an alcoholic solution of (1) codein, (2) resorcinol, (3) thymol and (4)  $\beta$ -naphthol. To each tube is added 0.4 ml. of the brominated sample and 0.1 ml. of a 4% solution of potassium bromide, then 2 ml. of conc. sulphuric acid. The tubes containing codein and  $\beta$ -naphthol are heated for 2 minutes in a water bath. The codein solution will show a blue tint; the resorcinol a blood-red colour becoming yellow-red on dilution with acetic acid; the thymol a wine-red colour becoming rose-red on dilution; and the  $\beta$ -naphthol will develop an emerald-green fluorescence. A more positive identification may be based upon the formation of glyceryl tribenzoate which has m.p. 72°. For this purpose 0.1 ml. of the specimen is shaken for 5 minutes with 0.4 ml. of benzoyl chloride and 5 ml. of 10% sodium hydroxide solution. After shaking, 10 ml. of cold water are added and the precipitated tribenzoate is filtered, washed and crystallised from 35% alcohol.

Provided that a sufficient amount of the sample is available, it is possible by distillation under reduced pressure to separate moderately pure glycerol, even from fairly complex mixtures.

#### QUANTITATIVE DETERMINATION OF GLYCEROL.

Here only the determination of glycerol in commercial products containing considerable quantities of it can be considered. The determination of glycerol in fermented liquors falls outside the scope of this article.

A direct method for determining glycerol in oils and fats by isolating it has been worked out by Shukoff and Schestakoff (*Z. angew. Chem.* 1905, **18**, 294; cf. Fachini and Dorta, *Boll. Chim. farm.* 1910, **49**, 237). It is necessary to operate with a solution containing at least 40% of glycerol. If the solution be more dilute, a quantity corresponding to about 1 g. of glycerol is carefully evaporated on the water-bath, the concentration not being increased to such a point that volatilisation of glycerol can take place (i.e. a concentration of about 50% must not be exceeded). Before evaporating, the solution is rendered slightly alkaline with potassium carbonate. The concentrated solution is then mixed with 20 g. of ignited and powdered anhydrous sodium sulphate and exhausted in a Soxhlet extractor with anhydrous acetone (previously well dried over anhydrous potassium carbonate). As acetone attacks both cork and indiarubber, all connections must be made with ground-glass fittings. The extraction requires several hours, and the results, at best, are only approximately correct.

As a rule, the determination of glycerol in oils and fats is carried out by one of the following indirect methods.

**Dichromate Process.**—This method which was first described by Hehner (*J.S.C.I.* 1889, **8**, 5) has displaced the older permanganate method of Wanklyn and Fox (*l.c.*, p. 80) and Benedikt and Zsigmondy (*l.c.*, p. 80). With due attention to the details as described on p. 61c, it affords a most reliable determination and has been often recommended as the standard method. It depends upon the complete oxidation of the

purified glycerol to carbon dioxide and water, but can be suitably applied only after removal of all organic impurities; see p. 61. The application of this method to various types of glycerin has been critically studied by S. Fachini and S. Somazzi (*Chim. et Ind.* 1924, Spec. No. (Paris 1923 Congress) 554S).

**Acetin Process.**—In case an impure glycerin be under examination (such as the crude glycerins described on p. 42), it is best to determine the proportion of glycerol by the Benedikt-Cantor acetin process, which is based on the quantitative conversion of glycerol into triacetin on heating the solution with acetic anhydride. If the product of this reaction is then dissolved in water, and the free acetic acid carefully neutralised with alkali, the dissolved triacetin can be readily estimated by saponification with a known volume of standard alkali, and titrating back the excess.

Details of the method are given in the Report of the International Committee on the Analysis of Glycerin (*see* p. 60b).

**Copper Process.**—A newer method of some promise has been put forward by Bertram and Rutgers (*Rec. trav. chim.* 1938, **57**, 681) and revised by the Glycerin Analysis Committee of the American Oil Chemists' Society (*Oil and Soap*, 1941, **18**, 14) which depends upon the formation of a glycerol-copper complex in an alkaline alcoholic solution.

Although the precision obtainable falls somewhat short of the standard required for commercial transactions, the method has the great advantage that it can be applied to impure preparations and mixtures without preliminary purification, and so affords a rapid and easy means of determining the approximate glycerol content of products grossly contaminated with substances which would interfere with the standard acetin or dichromate procedures, such as sugars, trimethylene glycol, diethylene glycol, glycol ethers (e.g., "cellosolve," "carbital") oxalic acids, or hydroxyacids such as tartaric and citric. None of these shows as much as 1% of apparent glycerol when tested by the new method: ethylene glycol, propylene glycol and hexahydric alcohols (mannitol, sorbitol) show from 2 to 5% apparent glycerol. Polyglyceryl ethers and alkylolamines interfere with the determination, but small quantities of ammonia do not. According to A.O.C.S. revised procedure, not more than 10 ml. of the glycerin solution, containing not more than 0.8 g. of glycerol, is weighed into a 100-ml. calibrated flask and diluted to 10 ml. with distilled water; 10 ml. of sodium hydroxide solution (30 g. per 100 ml.) are added, followed immediately by 60 ml. of 95 v/v% alcohol, and after mixing there is added (from a burette) an alcoholic solution of cupric chloride (10 g.  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  per 100 ml.) until a permanent undissolved precipitate of copper hydroxide remains after shaking; an excess of 0.5 ml. of the copper solution is added and the volume adjusted to 100 ml. with alcohol, and the solution shaken for at least a minute. (The solution is maintained at 20° throughout these operations.) At least 60 ml. of the well-mixed solution is centrifuged at 1,300 r.p.m. for about 10 min.,

tempered at 20°, and a 50 ml. aliquot of the clear decanted solution is transferred to a 300 ml. conical flask, diluted with 100 ml. of water, and made just acid with glacial acetic acid; 2 ml. excess of the acetic acid is added, and after cooling the mixture in ice, 10 g. of KI are added and the liberated iodine is immediately titrated with 0.1 *N*-sodium thiosulphate solution, using a starch indicator: just before the end-point, 2 g. of ammonium thiocyanate are added. The percentage of glycerol in the sample is given by the relation  $\frac{(T-B) \cdot N \cdot 18.41}{S}$  where *T* and *B*

are the titration figures for the sample and blank tests respectively, *N* is the normality of the thiosulphate solution and *S* the weight of the sample. If greater accuracy is required, a correction can be applied for the volume of the copper precipitate: in this case, the whole of the solution is centrifuged and the factor 18.41

becomes  $9.205 \times \frac{(100-0.5V)}{50}$  where *V* is the apparent volume of the precipitate after centrifuging.

**Chemically Pure Glycerin.**—The proportion of glycerol in *chemically pure glycerin* is most conveniently ascertained by determining the specific gravity (see tables on pp. 49, 50) or by oxidising the glycerol by means of dichromate, provided organic impurities be absent. This is ascertained in the following manner: A somewhat dilute solution is mixed with a cold ammoniacal silver nitrate solution; the solution should remain colourless even after standing for 24 hours. Any acrolein present in the sample is detected by the test described above. Any polyglycerols, due to faulty distillation, are determined by allowing an accurately weighed quantity of the sample to evaporate gently at 160°. Care should be taken not to heat too rapidly, otherwise even the purest glycerol may become polymerised with the production of the very substances that are to be detected. From the weight of the residue, the weight of ash, subsequently found on incineration, must be deducted. The difference (the "organic residue") is a fair indication of the care with which the glycerol has been manufactured.

The following Table XIII gives the "organic residue" and ash of a number of typical pure glycerins.

TABLE XIII.—ORGANIC RESIDUE AND ASH IN COMMERCIAL GLYCERINS.

Once distilled (dynamite) glycerin.				
No.	Residue at 160°, %.	Ash, %.	Organic residue, %.	Chloride, NaCl, %.
1	0.018	0.007	0.011	0.0013
2	0.013	0.005	0.008	0.0020
3	0.019	0.007	0.012	0.0022
4	0.020	0.009	0.011	0.0030
Double distilled (C.P.) glycerin.				
5	0.011	0.005	0.006	0.0013
6	0.014	0.009	0.005	0.0020
7	0.009	0.004	0.005	0.0010

Chemically pure glycerin must be free from all but the most minute traces of arsenic; the maximum content permitted by the British and United States Pharmacopœias is 4 and 10 p.p.m. respectively. This is ascertained by the Gutzeit test (v. Vol. I, 470b).

It should be neutral to litmus, leave no ash on ignition, and have sp.gr. of at least 1.260 at 15.5°. It should not emit any odour when heated on the water-bath, or any fruity odour when warmed with alcohol and sulphuric acid. It should not contain sulphates, chlorides, oxalates, metals or sugars, and when mixed with an equal volume of water must not reduce Barreswil's (Fehling's) solution. It should show at most a yellow coloration in Hager's test, according to which 5 ml. of the sample are mixed with 5 ml. of 26% ammonia solution and 5 drops of silver nitrate solution, and left in the dark for 15 minutes at the ordinary temperature.

The British Pharmacopœia (1932) requires glycerin to have sp.gr.<sub>15.5</sub> 1.260–1.265; to have not more than 0.01% of ash; to be free from reducing substances and fatty acids; and to contain not more than about 2 p.p.m. of iron, not more than 1 p.p.m. of lead and not more than 4 p.p.m. of arsenic.

**Distilled Glycerin (Dynamite Glycerin).**—The proportion of glycerol in these products is best determined by the acetin method. "Dynamite glycerin" is usually sold according to a specification agreed upon between buyer and seller. The following conditions are usually stipulated: sp.gr.<sub>15.5</sub> not below 1.262; neutral to litmus, light in colour, free from smell; ash not more than 0.05%; saponification equivalent not more than 0.1% as Na<sub>2</sub>O; salt not more than 0.01%; water not more than 1.5% and glycerol at least 98.5%. A test for reducing substances with silver nitrate is generally included and some well-known specifications include a test for the yield and separation on nitration. The latter test requires great care and is by no means always a reliable guide to the yield on the large scale.

#### ANALYSIS OF CRUDE GLYCERINS.

The *International Standard Acetin Method* still retains official status, although objections against it have been raised, both on account of the tedious procedure and a doubt as to the accuracy of the results. Many of the objections raised from time to time are, however, a result of inattention to the important details set out in the I.S.M. For example the use of well-boiled CO<sub>2</sub>-free water is essential to accuracy. The committee of the American Oil Chemists' Society (Oil and Fat Ind. 1931, 8, 297; Oil and Soap, 1933, 10, 71) report that the figures obtained by the dichromate method agree better with those deduced from the specific gravity (Bosart-Snoddy) than do the results of the acetin method.

#### *International Standard Methods.*<sup>1</sup>

**"Analysis of Crude Glycerol.**—The valuation of crude glycerol has assumed great commercial importance owing to the value of the

<sup>1</sup> Analyst, 1911, 36, 314.

commodity. The want of uniformity in the methods and processes of analysis, together with the irregularity of the results obtained, emphasised the desirability for the standardisation of crude glycerol analysis; so with this object in view committees were formed in America, France, Germany, and Great Britain. These committees worked in the first instance independently, but were ultimately brought together, and after a series of conferences the conclusions arrived at by the various committees were summarised, and drawn up in the form in which they are now presented. The methods detailed in this report have the unanimous support of each of the above committees, and are strongly recommended by them as International Standards.

**"Sampling.**—The most satisfactory method available for sampling crude glycerol liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerol sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler (a suitable sampling apparatus is described in an appendix to the report), brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate. Each drum must be sampled. Glycerol which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerol to be taken, including any deposit.

**"Analysis.**—(1) *Determination of Free Caustic Alkali.*—Weigh 20 g. of the sample into a 100 ml. flask, dilute with approximately 50 ml. of freshly-boiled distilled water, add an excess of neutral barium chloride solution, 1 ml. of phenolphthalein solution, make up to the mark, and mix. Allow the precipitate to settle, draw off 50 ml. of the clear liquid, and titrate with N-acid. Calculate to percentage of  $\text{Na}_2\text{O}$  existing as caustic alkali.

**"(2) Determination of Ash and Total Alkalinity.**—Weigh 2–5 g. of the sample in a platinum dish, burn off the glycerol over a luminous Argand burner, or other source of heat giving a low flame-temperature, the temperature being kept low to avoid volatilisation, and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixiviate with hot distilled water, filter, wash and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate and carefully ignite without fusion. Weigh the ash. Dissolve the ash in distilled water, and titrate total alkalinity, using as indicator methyl orange cold, or litmus boiling.

**"(3) Determination of Alkali present as Carbonate.**—Take 10 g. of the sample, dilute with 50 ml. distilled water, add sufficient N-acid to neutralise the total alkali found at (2), boil under a reflux condenser for 15–20 minutes,

wash down the condenser tube with distilled water free from carbon dioxide and titrate back with N/1-NaOH, using phenolphthalein as indicator. Calculate the percentage of  $\text{Na}_2\text{O}$ . Deduct the  $\text{Na}_2\text{O}$  found in (1). The difference is the percentage of  $\text{Na}_2\text{O}$  existing as carbonate.

**"(4) Alkali combined with Organic Acids.**—The sum of the percentage of  $\text{Na}_2\text{O}$  found at (1) and (3) deducted from the percentage found at (2) is a measure of the  $\text{Na}_2\text{O}$  or other alkali combined with organic acids.

**"(5) Determination of Acidity.**—Take 10 g. of the sample, dilute with 50 ml. of distilled water free from carbon dioxide, and titrate with N/1-NaOH and phenolphthalein. Express in terms of  $\text{Na}_2\text{O}$  required to neutralise 100 g.

**"(6) Determination of Total Residue at 160°.**—For this determination the crude glycerol should be slightly alkaline with  $\text{Na}_2\text{CO}_3$ , not exceeding the equivalent of 0.2%  $\text{Na}_2\text{O}$ , in order to prevent loss of organic acids. To avoid formation of polyglycerol, this alkalinity must not be exceeded.

**"Preparation of Glycerin.**—10 g. of the sample are weighed into a 100 ml. flask, diluted with water, and the calculated quantity of N/1-HCl or  $\text{Na}_2\text{CO}_3$  added to give the required degree of alkalinity. The flask is filled to 100 ml., the contents mixed and 10 ml. measured into a weighed Petri or similar dish 2.5 in. diameter and 0.5 in. deep, which should have a flat bottom (and rounded connection with the sides). In the case of crude glycerins abnormally high in organic residue a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30–40 mg.

**"Evaporation of the Glycerol.**—The dish is placed on a water-bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 in. cube, having an iron plate  $\frac{3}{4}$  in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf half-way up the oven. On these strips the dish containing the glycerol is placed. The bulb of the thermometer should also rest upon one of the strips.

"If the temperature of the oven has been adjusted to 160° with the door closed, a temperature of 130–140° can be readily maintained with the door partially open, and the glycerol, or most of it, should be evaporated off at this temperature.<sup>1</sup> When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

"An addition of 0.5–1 ml. of water is made, and by a rotatory motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water-bath or top of the oven until the excess water has evaporated and the residue is in such condition that on returning to the oven at 160° it will not spit. The time taken up to this point cannot be definitely given, nor is it of importance. Usually 2–3 hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in

<sup>1</sup> See note by Grimwood mentioned on p. 62c.

the oven, the temperature of which is carefully maintained at 160° for 1 hour, when it is removed, cooled, the residue treated with water and the water evaporated as before. The residue is then subjected to a second baking of 1 hour, after which the dish is allowed to cool in a desiccator over sulphuric acid, and weighed. The treatment with water, etc., is repeated until a constant loss of 1-1.5 mg. per hour is obtained.

*"Corrections to be Applied to the Weight of Total Residue."*—In the case of acid glycerol, a correction must be made for the alkali added. One ml. N/1-alkali represents an addition of 0.022 g. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na<sub>2</sub>CO<sub>3</sub> to NaCl. The corrected weight multiplied by 100 gives the percentage of *total residue* at 160°.

"Preserve the total residue for the determination of the non-volatile acetylisable impurities.

"(7) *Organic Residue.*—Subtract the ash from the total residue at 160°. (*Note.*—It should be noted that alkaline salts of organic acids are converted to carbonates on ignition, and that the CO<sub>2</sub> radiate thus derived is not included in the organic residue.)

"(8) *Moisture.*—This test is based on the fact that glycerol can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphoric anhydride. 2-3 g. of very bulky asbestos freed from acid-soluble material, which has previously been dried in a water-oven, are placed in a small stoppered weighing-bottle of about 15 c.c. capacity. The weighing-bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1-2 mm. of mercury, until constant in weight. From 1 to 1.5 g. of the sample is then carefully dropped on to the asbestos in such a way that it will be all absorbed. The weight is again taken, and the bottle replaced in the desiccator under 1-2 mm. pressure until constant in weight. At 15° the weight is constant in about 48 hours. At lower temperatures the test is prolonged. (*Note.*—A blank similarly prepared from glycerol free from glycols and dried until anhydrous *in vacuo* over sulphuric acid is kept with the test sample and any loss in weight of the anhydrous blank may be deducted from the amount lost by the sample. If glycols are present in the crude glycerins under test the blank may slightly increase in weight.)

"The sulphuric acid in the desiccator must be frequently renewed.

*"Acetin Process for Glycerol Determination."*—This process is the one agreed upon at a Conference of Delegates from the American, British, French and German Committees, and has been confirmed by each of the above Committees as giving results nearer to the truth on crudes in general, and is the process to be used (if applicable) whenever only one method is employed. On pure glycerols the results are identical with those of the dichromate process. For the application of this process the crude glycerol should not contain over 50% water.

"The following reagents are required :

"(A) *Best Acetic Anhydride.*—This should be carefully selected. A good sample must not require more than 0.1 ml. normal NaOH for saponification of the impurities when a blank is run on 7.5 ml. Only a slight colour should develop during digestion of the blank.

"(B) *Pure Fused Sodium Acetate.*—The purchased salt is again completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or a desiccator. It is most important that the sodium acetate be anhydrous.

"(C) *A Solution of Caustic Soda for Neutralising, of about N/1-Strength, free from Carbonate.*—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide), and allowing to settle until clear, or filtering through asbestos (in the absence of carbon dioxide). The clear solution is diluted with water free from carbon dioxide to the strength required.

"(D) *N/1 Caustic Soda, free from Carbonate.*—Prepared as above, and carefully standardised.

"Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

"(E) *N/1 Acid.*—Carefully standardised.

"(F) *Phenolphthalein Solution.*—0.5% phenolphthalein in alcohol and neutralise.

"*THE METHOD.*—Into a narrow-mouthed flask (preferably round-bottomed), capacity about 120 ml., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25-1.5 g. of the glycerol. Add first about 3 g. of the anhydrous sodium acetate, then 7.5 ml. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9-10 mm. diameter.

"The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used, it should have had a preliminary treatment with hot acetic anhydride vapour.

"Heat the contents and keep just boiling for 1 hour, taking precautions to prevent the salts drying on the sides of the flask. Allow the flask to cool somewhat, and through the condenser tube add 50 ml. of the carbon-dioxide-free distilled water, heated to about 80°, taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapours from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify, and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80°, until the solution is complete, except a few dark flocks representing organic impurities in the crude. By giving the flask a rotatory motion solution is more quickly effected. Cool the flask and contents without loosening from condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off stopper

or ground glass connection into the flask and filter contents of flask through an acid-washed filter into a Jena glass flask of about 1 litre capacity: the filtrate should amount to about 200 ml. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 ml. of phenolphthalein solution (F), then run in a caustic soda solution (C) or (D) until a faint pinkish-yellow colour appears throughout the solution. This neutralisation must be done most carefully. The alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling, with occasional agitation or change of motion, until the solution is nearly neutralised, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon-dioxide-free water, and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

"Now run in from a burette 50 ml. or a calculated excess of  $N/1\text{-NaOH}$  (D) and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate excess of  $\text{NaOH}$  with  $N/1\text{-acid}$  (E) until the pinkish-yellow or chosen end-point colour just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end-point taken.

"From the  $N/1\text{-NaOH}$  consumed calculate the percentage of glycerol after making the correction for the blank test described below.

"1 ml. of  $N/1\text{-NaOH}$  = 0.03069 g. of glycerol. The coefficient of expansion for normal solutions is approximately 0.00033 per ml. for each degree C. A correction should be made on this account if necessary.

"*Blank Test.*—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analysis. After neutralising the acetic acid it is not necessary to add more than 5 ml. of the  $N/1\text{-alkali}$  (D), as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination.

"*Determination of the Glycerol Value of the Acetylisable Impurities.*—The total residue at  $160^\circ$  is dissolved in 1 or 2 ml. of water, washed into a clean acetylising flask, 120 ml. capacity, and the water evaporated. Now add anhydrous sodium acetate and proceed as in the glycerol determinations before described. Calculate the result to glycerol.

"*Analysis of the Acetic Anhydride.*—Into a weighed stoppered vessel, containing 10–20 ml of water, run about 2 ml. of the anhydride, replace stopper and weigh; allow to stand with occasional shaking for several hours, until all anhydride is hydrolysed; then dilute to about 200 ml., add phenolphthalein and titrate with  $N/1\text{-NaOH}$ . This gives the total acidity due to free acetic acid and acid formed from anhydride.

"Into a stoppered weighing-bottle containing

a known weight of recently distilled aniline (from 10–20 ml.) measure about 2 ml. of the sample, stopper, mix, allow to cool and weigh. Wash contents into about 200 ml. of cold water and titrate acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one half the acid due to anhydride the other half having formed acetic anhydride; subtract the second result from the first (both calculated for 100 g.) and double result, obtaining ml.  $N/1\text{-NaOH}$  per 100 g. sample. One ml.  $\text{NaOH}$  equals 0.0510 g. of acetic anhydride.

"*Bichromate Process for Glycerol Determination.*—*Reagents Required:* (a) *Pure Potassium Bichromate* powdered and dried in air free from dust or organic vapours at  $110\text{--}120^\circ$ . This is taken as the standard.

"(b) *Dilute Bichromate Solution.*—7.4564 g. of the above bichromate (a) are dissolved in distilled water and the solution made up to a litre at  $15.5^\circ$ .

"(c) *Ferrous Ammonium Sulphate.*—Dissolve 3.7282 g. of potassium dichromate (a) in 50 ml. of water. Add 50 ml. of 50% (by volume) sulphuric acid and to the cold undiluted solution add from a weighing-bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute dichromate (b). Calculate the value of the ferrous salt in terms of dichromate.

"(d) *Silver Carbonate.*—This is prepared as required for each test from 140 ml. of 0.5% silver sulphate solution by precipitation with about 4.9 ml.  $N\text{-sodium carbonate}$  solution (a little less than the calculated quantity of  $N\text{-sodium carbonate}$  should be used; any excess of alkali carbonate prevents rapid settling), settle, decant and wash once by decantation.

"(e) *Lead Subacetate.*—Boil a pure 10% lead acetate solution with an excess of litharge for 1 hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

"(f) *Potassium Ferricyanide.*—A very dilute solution containing about 0.1%.

"*THE METHOD.*—Weigh 20 g. of the glycerol, dilute to 250 ml. and take 25 ml. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and then add a slight excess (about 5 ml. in most cases) of the basic lead acetate (e), allow to stand a few minutes, dilute with distilled water to 100 ml. and then add 0.15 ml. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 ml. and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 ml. is ample. Occasionally a crude glycerol will be found requiring more, and in this case another aliquot of 25 ml. of the dilute glycerol should be taken and purified with 6 ml. of the basic acetate. Care must be taken to avoid a marked excess of basic acetate.) Measure off 25 ml. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid

(1.4) to precipitate the small excess of lead as sulphate. Add 3.7282 g. of the powdered bichromate (a). Rinse down the bichromate with 25 ml. of water and stand, with occasional shaking, until all the bichromate is dissolved (no reduction will take place).

"Now add 50 ml. of 50% sulphuric acid (by volume), and immerse the vessel in boiling water for 2 hours, and keep protected from dust and organic vapours, such as alcohol, until the titration is completed. Add from a weighing-bottle a slight excess of the ferrous ammonium sulphate (c), making spot tests on a porcelain plate with the potassium ferrieyanide (f). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

"1 g. glycerol equals 7.4564 g. bichromate.

"1 g. bichromate equals 0.13411 g. glycerol.

"Notes.—(1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

"(2) Before the bichromate is added to the glycerol solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

"(3) For 'crudes' practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0.5 ml.

"(4) It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate.

"Instructions for Calculating Actual Glycerol Content.—(1) Determine the apparent amount of glycerol in the sample by the acetin process as described. The result will include acetylisable impurities if any be present.

"(2) Determine the total residue at 160°.

"(3) Determine the acetin value of the residue at (2) in terms of glycerol.

"(4) Deduct the result found at (3) from the percentage obtained at (1), and report this corrected figure as glycerol. If volatile acetylisable impurities are present, these are included in this figure.

"Notes and Recommendations.—Experience has shown that in crude glycerol of good commercial quality the sum of water, total residue at 160° and corrected acetin result, comes to within 0.5 of 100. Further, in such 'crudes' the bichromate result agrees with the uncorrected result to within 1%.

"In the event of greater differences being found, impurities such as polyglycerols or trimethylene glycol are present.

"In valuing crude glycerol for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites and thiosulphates. The methods for detecting and determining these impurities have not formed the subject of this investigation.

"Recommendations by Executive Committee.—If the non-volatile organic residue at 160° in the case of a soap lye 'crude' be over 2.5%—i.e. when not corrected for carbon dioxide in the ash—then the residue shall be examined by the acetin method and any excess of glycerol

found over 0.5% shall be deducted from the acetin figure." (Cf. footnote to Table I, p. 45.)

"In the case of saponification, distillation and similar glycerol the limit of organic residue which should not be passed without further examination shall be fixed at 1%. In the event of the sample containing more than 1%, the organic residue must be acetylated, and any glycerol found (after making the deduction of 0.5%) shall be deducted from the percentage of glycerol found by the acetin test."

With reference to this Report, Grimwood (J.S.C.I. 1913, 32, 1039) has shown that the oven recommended therein does not enable a steady temperature to be maintained. In the case of one oven he found a maximum variation of 45° between the temperatures of two shelves. In place of the standard oven he has devised an electrically heated oven cased with urallite. He also describes an accelerated method of evaporating the glycerin, in which the vapours are removed by means of an electric fan.

**Standard Specifications for Soap Lye and Saponification Crude Glycerins.**—The following standard specifications were drawn up by the British Executive Committee on Crude Glycerin Analysis, and approved at a meeting of glycerin makers, buyers and brokers held in London on October 3, 1912:

**Soap Lye Crude Glycerin.**—Analysis to be made in accordance with the International Standard Methods. *Glycerol.*—The Standard shall be 80% of glycerol. Any crude glycerin tendered which tests 81% of glycerol or over, shall be paid for at a *pro rata* increase, calculated as from the standard of 80%. Any crude glycerin which tests under 80% of glycerol, but is 78% or over shall be subject to a reduction of 1½ times the shortage, calculated at the *pro rata* price as from 80%. If the test falls below 78% the buyer shall have the right of rejection. *Ash.*—The standard shall be 10%. In the event of the percentage of ash exceeding 10%, but not exceeding 10.5%, a percentage reduction shall be made for the excess calculated as from 10% at *pro rata* price, and if the percentage of ash exceeds 10.5%, but does not exceed 11%, an additional percentage reduction shall be made equal to double the amount in excess of 10.5%. If the amount exceeds 11% the buyer shall have the right to reject the parcel.

**Organic Residue.**—The standard shall be 3%. A percentage deduction shall be made of 3 times the amount in excess of the standard of 3%, calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 3.75%.

**Saponification Crude Glycerin.**—Analysis to be made in accordance with the International Standard Methods. *Glycerol.*—The standard shall be 88%. Any crude glycerin which tests 89% or over shall be paid for at a *pro rata* increase calculated as from the standard of 88%. Any crude glycerin which tests under 88%, but is 86% or over, shall be subject to a reduction of 1½ times the shortage, calculated at *pro rata* price as from 88%. If the test falls below 86%, the buyer shall have the right of rejection. *Ash.*—The standard

shall be 0.5%. In the event of the percentage of ash exceeding 0.5%, but not exceeding 2.0%, a percentage reduction shall be made equal to double the amount in excess of 0.5%. If the amount of ash exceeds 2.0% the buyer shall have the right to reject the parcel.

**Organic Residue.**—The standard shall be 1%. A percentage deduction shall be made of twice the amount in excess of the standard of 1%, calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 2%.

**Glycols in Glycerin.**—Rayner (J.S.C.I. 1926, 45, 265T) has shown that *trimethylene glycol*,  $\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b.p. 210–211°, sp.gr. 20°/20° 1.0554 (Cocks and Salway, *ibid.* 1922, 41, 17T) may be formed by bacterial fermentation (*cf.* “*Citrobacter sp.*,” Werkman and Gillen, J. Bact. 1932, 23, 167) when dilute crude glycerin lyes are stored for long periods. Rayner states that small amounts of the glycol are not objectionable in glycerin intended for nitration, but if the crude contains considerable quantities (*e.g.* 2–3%) it is difficult to manufacture a dynamite glycerin of the requisite density.

#### DETERMINATION OF GLYCOLS.

Since the standard methods for glycerin analysis were agreed upon in 1911, and later accepted as International Standard Methods, it has been found possible to devise means for the estimation of the glycols present in crude glycerin. In addition to *trimethyleneglycol* (1:3-dihydroxypropane), crude glycerin is known to contain 1:2-dihydroxypropane, and other glycols are probably also present. An accurate method for the quantitative differentiation between the 1:3- and the 1:2-dihydroxypropanes is not available, but the method described below, which is substantially that of Cocks and Salway (J.S.C.I. 1922, 41, 17T) represents a substantially accurate means of determining the total amount of the glycols present in crude glycerin.

100 g. of the original sample are weighed into a 400 ml. distillation flask, to which is attached an air condenser (3 ft. long) connected to a 100 ml. receiving vessel. The distillation flask is also fitted with the usual glass tube drawn to a fine capillary and the distillation is carried out at approximately 30 mm. pressure. If troublesome frothing occurs it can be checked by the addition of hydrochloric acid to faint acidity. The heating should be so regulated that distillation proceeds at the rate of 1 drop per second. Approximately 30% is distilled, the receiving flask having been previously roughly calibrated, but the exact weight of the distillate is ascertained at the end of the distillation.

If any priming has occurred during distillation, the distillate must be completely re-distilled. The specific gravity of the distillate at 20°/20° is determined, and the percentage of acetylisable compounds calculated as glycerol is ascertained by the acetin test.

**Method of Calculation.**—The sp.gr. at 20°/20° of a glycerin corresponding to the acetin value of the distillate as found above is ascertained from specific gravity tables (*cf.* Tables III and

pp. 49, 50). From this is deducted the specific gravity of the distillate actually found by experiment, and the result is divided by a variable factor obtained from Table XIV. The quotient returns the percentage of glycols calculated as trimethylene glycol in the distillate, from which the percentage in the original sample may be computed. For example:

100 g. of the crude glycerin gave 35 g. of distillate having a sp.gr. of 1.1865 at 20°/20°. The acetin value of the distillate corresponded to an apparent glycerol content of 77.4%, and the appropriate factor (*see* Table XIV) is 0.00161.

The sp.gr. at 20°/20° of a glycerol of 77.4% concentration is 1.2038 (*see* Table III): hence the percentage of trimethylene glycol in the distillate

$$= \frac{1.2038 - 1.1865}{0.00161} = 10.7\%.$$

and the percentage of trimethylene glycol in the original crude glycerin

$$= \frac{10.7 \times 35}{100} = 3.75\%.$$

TABLE XIV.—FACTORS FOR USE IN THE CALCULATION OF GLYCOL CONTENT.

Acetin value, %.	Factor.
50	0.00134
55	0.00139
60	0.00144
65	0.00149
70	0.00154
75	0.00159
80	0.00164
85	0.00169
90	0.00174
95	0.00179

An alternative method for the determination of glycols is afforded by Fachini and Somazzi's process (Ind. Oli e. Grassi, 1923, Nos. 2, 6, 10; *cf.* Chem. Trade J. 1923, 73, 127, 702; *Chim. et Ind.*, 1924, Spec. No., p. 118D). These authors determine the apparent glycerol content by the dichromate titration method which is suitably modified so that the carbon dioxide evolved by the oxidation may be collected and weighed. From a consideration of the two relations:

- (1)  $\text{C}_3\text{H}_8(\text{OH})_3 + 7\text{O} = 3\text{CO}_2 + 4\text{H}_2\text{O}$ , and
- (2)  $\text{C}_3\text{H}_8(\text{OH})_2 + 8\text{O} = 3\text{CO}_2 + 4\text{H}_2\text{O}$

it is evident that the glycol content can be readily calculated from the dichromate figure and the amount of carbon dioxide produced. The value of this method for the analysis of crude glycerins is confirmed by Berth (Seifens.-Ztg. 1929, 56, 269, 279).

#### USES OF GLYCERIN.

Besides the well-established use of glycerin for dynamite manufacture and in the preparation of tobacco and in pharmacy, a few of the recent applications of glycerin in the arts may be briefly mentioned (*see also* Darke and Lewis,

## GLYCERIN.

Chem. and Ind. 1928, 6, 1073; J. W. Lawrie, "Glycerol and the Glycols," New York, 1928).

**Alkyd ("Glyptal") Resins.**—Glycerin may be condensed (esterified) by heating with phthalic acid (or anhydride) (cf. Van Bemmelen, 1856; Callahan, U.S.P. 1108329/1914) to yield fluid products which polymerise and resinify as the heating is continued. These form moderately soluble "heat-convertible" ("green") resins, which can be transformed into hard insoluble and infusible resins by baking. If part of the phthalic acid is replaced, e.g. by succinic acid, more soluble flexible resins are obtained. If drying oil fatty acids are incorporated, a class of "oxygen-convertible" or "oil-modified glyptal resins" can be prepared; these are soluble in drying oils and solvent naphtha, forming varnishes which dry to hard resistant films on exposure to air (cf. Kienle, Ind. Eng. Chem. 1929, 21, 349). These glyptal resins are extensively used in lacquers, air-drying or baking varnishes, insulating and petrol-proof varnishes, adhesives, etc., and also for small moulded articles.

Glycerin is used as a moistening and preserving agent in many food products and in the manufacture of printer's roller compositions and various inks. It has been applied successfully as a drying agent for town-gas (cf. Knecht and Muller, J.S.C.I. 1924, 43, 177T), and for a time it was used in France as a dehydrating agent for alcohol (Mariller and Granger process: cf. Pique, Chim. et Ind. Spec. No. 1925, 2108; Chim. et Ind. 1928, 19, 396 (84T); Mariller and Granger, Admn. P. 27171 and 25633 to F.P. 512653; Van Ruymbeke, F.P. 539103). Glycerin solutions have been suggested for steel-quenching (v. Scott, Trans. Amer. Soc. Steel Treating, 1924, 6, 13).

Glycerin is widely used to provide circulating non-freezing solutions, e.g. for motor-car radiators; such solutions may with advantage contain small amounts of anti-oxidants and even when supercooled freeze without producing dangerous pressures by expansion.

The figures in the following Table XV of the freezing points of glycerol solutions are taken from Lane (Ind. Eng. Chem. 1925, 17, 924).

TABLE XV.—FREEZING POINT OF GLYCEROL SOLUTIONS (Lane).

% Glycerol (by weight).	F.p. °C	% Glycerol (by weight)	F.p. °C	% Glycerol (by weight).	F.p. °C.
11.5	— 2.0	64.0	—41.5	70.9	—37.5
22.6	— 6.0	64.7	—42.5	75.0	—29.8
25.0	— 7.0	65.6	—44.5	75.4	—28.5
33.3	—11.0	66.0	—44.7	79.0	—22.0
44.5	—18.5	66.7	—46.5	84.8	—10.5
50.0	—23.0	67.1	—45.5	90.3	— 1.0
53.0	—26.0	67.3	—44.5	95.3	+ 7.5
60.4	—35.0	68.0	—44.0	98.2	+13.5

Glycerol solutions can be much supercooled without crystallisation taking place; seeding is usually necessary. But as stated above, large

quantities of glycerol will solidify when left undisturbed for long periods at low temperatures.

A paste made by moistening litharge with glycerol sets rapidly without contraction to a hard cement-like mass. By selecting suitable proportions, and diluting with other oxides, fuller's earth, etc., the setting-time can be varied, and a series of useful cements and luting-compounds prepared (cf. Stäger, Z. angew. Chem. 1929, 42, 370; Gleason, Paper Trade J. 1932, 95, T.A.P.P.I. Sect. 169; Neville, J. Physical Chem. 1926, 30, 1181).

For many of these purposes, including nitration, ethylene glycol may be substituted for glycerol, and should the price of the latter increase the glycol may prove a serious rival (v. DYNAMITE, Vol. IV, 242d).

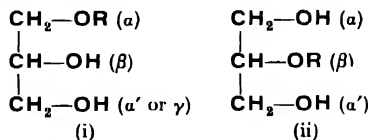
### DERIVATIVES OF GLYCEROL.

For compounds of glycerol with metal oxides, see p. 56c.

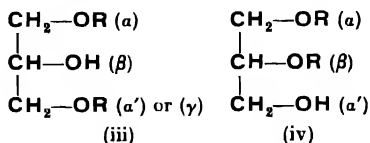
**Esters of Glycerol.**—As a trihydric alcohol, glycerol is capable of forming esters with organic or inorganic acids, or esters containing both inorganic and organic acid residues.

**Organic Esters of Glycerol**—(*Glycerides*.—The most important esters of glycerol with organic acids are the tri-esters—*triglycerides*—resulting from the combination of the three hydroxyl groups of the glycerol molecule with 3 mol. of a higher monobasic fatty acid, which form the characteristic and principal components of the natural oils and fats of animal or vegetable origin.

By the esterification of only one, or two, of the three hydroxyl groups, glycerol forms mono- and di-acid esters respectively, which, in the case of the fatty acid esters, are usually referred to as *monoglycerides* and *diglycerides*. As would be expected from the constitution of glycerol, two structurally isomeric monoglycerides may exist, according to the position which the acid radical occupies in the molecule. This is indicated in the formulæ (i) and (ii), in which R represents the acid radical. Monoglycerides corresponding to these formulæ are termed  $\alpha$ - and  $\beta$ -monoglycerides respectively.



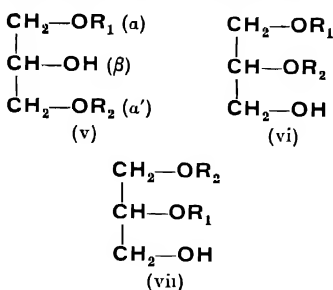
When a second fatty acid radical enters the molecule, *diglycerides* are obtained: if both acid radicals are alike, two isomers are possible, viz. the symmetrical  $\alpha\alpha'$  (or  $\alpha\gamma$ ) (iii) and the  $\beta\beta$  (iv) diglyceride:



If the two acid radicals are different, three



isomers (v), (vi) and (vii) are possible, which may be termed "mixed diglycerides":



The  $\alpha$ -monoglycerides (i), the  $\alpha\beta$ -diglycerides (iv) and the three mixed diglycerides contain an asymmetric carbon atom, so that, theoretically, two optical isomers are possible in each of these cases, and the ordinary synthetically prepared inactive compounds presumably represent racemic forms.

Grun and Limpacher (Ber. 1927, 60 [B 255; cf. *ibid.* 266] have succeeded in resolving the sulphuric ester of  $\alpha\beta$ -distearin into two fractions by means of the brucine or strychnine salts; the potassium salt of the recovered distearin sulphate exhibited optical activity in cold solution, although the distearin prepared from it was entirely inactive.

Abderhalden (Ber. 1915, 48, 1847) and Ber munn *et al.* (Z. physiol. Chem. 1924, 137, 27, 4) have synthesised amino- $\alpha\beta$ -diglycerides (diacylaminopropanes) which could be resolved into optical antipodes, from which in turn very slightly optically active  $\alpha\beta$ -diglycerides were obtained. Optically active mono- and diglycerides have also been synthesised from *d*-(+)-acetone-glycerol by H. O. L. Fischer and Baer (Naturwiss. 1937, 25, 588; Baer and H. O. L. Fischer, J. Biol. Chem. 1939, 128, 479).

If one or more of the fatty acids concerned is (are) optically active—riemolonic, chaulmoogric or hydnoearpic acids, for example—they confer optical activity on their glycerides, apart from any consideration of the configuration of the acyl groups within the glyceride molecule.

Mono- and di-glycerides do not appear to occur in natural fresh fats, but very strong evidence has been adduced to show that these esters are formed in the course of slow hydrolysis of the natural triglycerides; hence they may be found in fats and oils which have become rancid by a natural process on exposure to air, light and moisture.

*Diacetin*, the diglyceride of acetic acid which finds some use as a solvent is discussed in the article ACETIN.

All the tri-esters of glycerol (the *triglycerides* or *fats*) may exhibit stereo-isomerism; the following varieties exist in the natural fats: one form of simple triglyceride,  $\text{C}_3\text{H}_5(\text{OR})_3$  in which all the acid radicals are alike; two types of isomeric mixed triglycerides in which two of the three acid radicals are identical (*e.g.*  $\alpha$ -oleodistearin and  $\beta$ -oleodistearin); and three isomeric mixed triglycerides in which all three fatty acid radicals are different.

Although theoretically any triglycerides containing an asymmetric carbon atom may exist in optically active isomeric forms, such active glycerides have never been found in the natural fats as recovered from animal or vegetable tissues; in all the known cases of optically active oils, *e.g.* castor oil (*q.v.*), chaulmoogra oil (*q.v.*), the activity is due to the presence of optically active fatty acids combined in the glycerides. B. Suzuki, however, suggests (Proc. Imp. Acad. Tokyo, 1930, 6, 71; 1931, 7, 222) that in the living animal the glycerides may be optically active, but that racemisation sets in very rapidly after the death of the tissues and extraction of the fat.

#### PREPARATION OF GLYCERIDES.

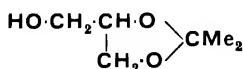
$\alpha$ -Monoglycerides and  $\alpha\alpha'$ -diglycerides may be prepared by treating the corresponding  $\alpha$ -monochlorohydrin and  $\alpha\alpha'$ -dichlorohydrin respectively (or the corresponding bromo- or iodo-hydrins) with the sodium, potassium or silver salts of the desired fatty acids (Guth, Z. Biol. 1902, 44, 8; Krafft, Ber. 1903, 36, 4339). Mixed diglycerides are obtained by treating an  $\alpha$ -acyl- $\alpha'$ -chlorohydrin with the potassium salt of the second fatty acid (Grun and Skopnik, *ibid.* 1909, 42, 3750). By treating diglycerides with an acyl chloride, a third fatty acid radical may be introduced into the molecule. Simple triglycerides are also formed (together with some di- and mono-glyceride) by heating glycerol with excess of the fatty acid (Berthelot, Ann. Chim. Phys. 1854, [iii], 41, 216, 240; cf. Schein, Rec. trav. chim. 1899, 18, 169); by heating the sodium or silver salt of the fatty acid with tribromohydrin (Guth, *l.c.*; cf. Partheil and Von Velsen, Arch. Pharm. 1900, 238, 261, 267) or by heating mono- or diglycerides with a further quantity of the fatty acid in question.

The workers mentioned above also attempted to produce  $\beta$ -monoglycerides and  $\alpha\beta$ -diglycerides by methods analogous to the above, *e.g.* starting from  $\beta$ -chlorohydrin, or by introducing a fatty acid radical (by means of the fatty acid chloride) into the  $\beta$ -position of an  $\alpha$ -acyl- $\alpha'$ -chlorohydrin and then hydrolysing the  $\alpha'$ -chlorine atom.

It has been proved, however, by E. Fischer that, in reactions involving mono- and diglycerides, there is a strong tendency for the acyl (or ether) radical to enter the glycerol molecule in the  $\alpha$ -position, whenever possible; further, migration of an existing  $\beta$ -acyl group to an adjacent vacant  $\alpha$ -position occurs very readily. It is clear from the work of Fischer and his successors that, in most cases, mixtures of  $\alpha$ - and  $\beta$ -monoglycerides were recovered by the earlier workers from syntheses designed to produce  $\beta$ -glycerides: similarly, most of the " $\alpha\beta$ -glycerides" recorded in the early literature (prepared, for example, from  $\alpha\beta$ -dichlorohydrin and fatty acid salts), must have been  $\alpha\alpha'$ -diglycerides, or (at best) mixtures of the  $\alpha\alpha'$ - and  $\alpha\beta$ -isomerides. Fischer and Bergmann finally devised a series of very mild reactions, to be performed in the cold, by which authentic  $\alpha$ -,  $\alpha\alpha'$ - and  $\alpha\beta$ -glycerides can be prepared. For the first syntheses of authentic  $\beta$ -monoglycerides, see Helferich and Sieber (Z. physiol. Chem. 1927,

170, 31; 1928, 175, 311); Bergmann and Carter (*ibid.* 1930, 191, 211).

The starting-point of many of these syntheses is "acetone-glycerol" ( $\alpha\beta$ -isopropylidene ether of glycerol)



or  $\alpha\beta$ - or  $\alpha\gamma$ -benzylidene glycerol. Fatty acid radicals are introduced by interaction of the free hydroxyl group with the appropriate acyl chloride in the presence of quinoline or pyridine (see E. Fischer, M. Bergmann and Barwind, *Ber.* 1920, 53 [B], 1589, 1606, 1621; Bergmann *et al.*, *ibid.* 1921, 54 [B], 936; *Z. physiol. Chem.* 1924, 137, 27, 47; Fairbourn, *J.C.S.* 1926, 3148; Fairbourn *et al.*, *ibid.* 1926-32; Hibbert *et al.*, *J. Amer. Chem. Soc.* 1928 onwards; C. G. King *et al.*, *ibid.* 1932 onwards).

These methods have been extended by Helfferich and by P. E. Verkade and his collaborators, who have achieved syntheses of authentic  $\alpha$ - and  $\beta$ -monoglycerides,  $\alpha\alpha'$ - and  $\alpha\beta$ -diglycerides and of mixed triglycerides of known configuration by employing the "trityl" (triphenylmethyl) derivatives of glycerol as intermediate stages (*cf.* Verkade and Van der Lee and collaborators, *Proc. K. Acad. Wetensch. Amsterdam*, 1934, 37, 812; 1937, 40, 580; *Rec. trav. chim.* 1935, 54, 716; 1936, 55, 267; 1937, 56, 365, 613). (The work of Verkade, Helfferich and others is reviewed *in extenso* (with 42

references) and discussed by Verkade in *Fette u. Seifen*, 1938, 45, 457; *cf. also* F. A. Norris, *Oil and Soap*, 1940, 17, 257.)

The application of methods of deacylation and detritylation of mixed acyl-trityl-glycerides to the determination of the configuration of mono- and di-glycerides is discussed in the same paper (*cf. also* Verkade and Van der Lee, *Rec. trav. chim.* 1938, 57, 417 *et seq.*).

Another method for the synthesis of unsymmetrical simple diglycerides is described by Daubert and King (*J. Amer. Chem. Soc.* 1939, 61, 3328):  $\alpha$ -monosodium glyceroxide is treated with benzyl chloroformate, and the free hydroxyl groups in the resultant  $\alpha$ -carbobenzyloxyglycerol are acylated with an acyl halide in the presence of quinoline, and the ester so obtained is reduced catalytically to the  $\alpha\beta$ -diglyceride.

Pure triglycerides commonly exhibit the phenomenon of a so-called "double melting-point" which was originally noted by Chevreul: if a glyceride is examined shortly after having been melted and fairly rapidly cooled, it will be found to melt (wholly or partially) at a certain temperature, then to solidify again at a higher temperature, only to remelt on further heating. On the other hand, the *crystalline* glyceride obtained, for example, by crystallisation from solution, or a solidified specimen which has been allowed to stand for a considerable time after solidification, shows a single melting-point corresponding to the higher figure registered in the previous case (*cf.* Table XVI). This behaviour was ascribed by Duffy (*J.C.S.* 1853, 5,

TABLE XVI.—MELTING-POINTS OF PURE GLYCERIDES (Bömer and Linprich).

Glyceride.	Melting-point <sup>1</sup>	"Transition-point" <sup>2</sup>	Solidifying-point	Began to solidify.	Melting-point of glyceride heated above its "transition-point"
	°C.	°C.	°C.	°C.	°C.
Tristearin (from mutton tallow) . . . . .	73.2	55.5	53.5	58	73.6
$\alpha$ -Palmitodistearin <sup>3</sup> (from tallow) . . . . .	61.5	52.1	49.7	55	63.4
$\beta$ -Palmitodistearin <sup>3</sup> (from lard) . . . . .	68.4	52.2	50.0	55	68.5
Stearodipalmitin (from mutton tallow) . . . . .	58.1	(48)	45.9	52	58.5
Stearodipalmitin (from lard) . . . . .	58.3	48.2	45.9	53	58.8

<sup>1</sup> Determined by Polenske's method.

<sup>2</sup> *I.e.* lower melting-point.

<sup>3</sup> The reverse configurations assigned by Bömer to the palmitodistearins from tallow and lard respectively have been corrected in the light of later information.

197) and Heintz (*J. pr. Chem.* 1849, [i], 48, 382; 1854, [i], 63, 168; Poggendorff's *Ann. Phys. Chem.* 1854, 93, 43; *cf. also* Grün and Schacht, *Ber.* 1907, 40, 1778; 1912, 45, 3691; Bömer, *Z. Unters. Nahr. Genussm.* 1907, 14, 90, 97; 1909, 17, 353, 363) to the existence of two physical modifications of each individual glyceride: viz. an unstable (labile) low-melting modification and a stable, high-melting form. (Bömer also refers to the melting-point of the labile form as the "transition-point," but this nomenclature must be rejected, since the change

from the labile to the stable form may take place even in the solid state, albeit less rapidly than in the molten condition.)

Crystallisation of the stable modification is a slow process (*Le Chatelier* and Cavaignac, *Compt. rend.* 1913, 156, 589), and when the melted glyceride is rapidly chilled, it first solidifies in the labile form, which gradually changes into the stable modification if it is allowed to stand for a prolonged period in the solid state, or is warmed for some time a few degrees above the lower melting-point (*cf.* the m.p. of cocoa

butter (Vol. III, 235b)). Further evidence for the above view was given by the later experiments of Bömer and Limpricht (Z. Unters. Nahr. Genussm. 1913, **25**, 367, 373) and by the work of Renders, Doppler and Oberg (Rec. trav. chim. 1932, **51**, 917) on the existence of two crystalline modifications of cacao butter; and the existence not only of two, but of three polymorphic modifications of glycerides (cf. Duffy, *l.c.*; Othmer, Z. anorg. Chem. 1915, **91**, 237; Nicolet, J. Ind. Eng. Chem. 1920, **12**, 741; and Loskit, Z. physiol. Chem. 1928, A, **134**, 135) has been established by the X-ray investigations of Clarkson and Malkin (J.C.S. 1934, 666). The highest-melting so-called  $\beta$ -modification is the stable form referred to above, in which the glyceride crystallises from solution: the intermediate  $\alpha$ -form, obtained by fairly rapid cooling from a melt is crystalline, but the lowest-melting modification, obtained by very rapid cooling, is described by Malkin as not truly crystalline but as possessing rather the properties of a glass. The melting-points determined by Malkin for various simple triglycerides are shown in Table XVII (cf. Othmer, Loskit, *l.c.*).

TABLE XVII.—MELTING-POINTS (°C.) OF TRIGLYCERIDES (Clarkson and Malkin).

	$\beta$ -form.	$\alpha$ -form.	Glass. <sup>1</sup>
Tristearin (Octadecylin) .	71.5	65.0	54.5
Trimargarin (Heptadecylin) .	63.5	61.0	50.0
Tripalmitin (Hexadecylin) .	65.5	56.0	45.0
Tripentadecylin .	54.0	51.5	40.0
Trimyristin (Tetradecylin) .	57.0	46.5	33.0
Tritoldeylin .	44.0	41.0	25.0
Trilaurin (Dodecylin) .	46.4	35.0	15.0
Triundecylin .	30.5	26.5	1.0
Tricaprin (Decylin) .	31.5	18.0	-15.0
Tricaprylin (Octylin) .	9.8-10.1 <sup>2</sup>		

<sup>1</sup> These temperatures are not true melting-points, but are the means of a small melting-range: they usually vary by  $\pm 1^\circ$  (Clarkson and Malkin).

<sup>2</sup> Hirschberger, J. Amer. Chem. Soc. 1930, **61**, 3587.

In the case of other investigators who have only recorded two melting-points for each glyceride (as is general in the older literature), these correspond as a rule with the melting-points of the stable form and of Malkin's lowest-melting labile modification.

The property of "triple melting" was found to be general for all the simple triglycerides examined from tricaprins to tristearins. In the case of the labile modifications, smooth curves are obtained on plotting the melting-points against the number of carbon atoms in the fatty acid concerned: the melting-points of the stable form, however, show an alternating or zig-zag progression (cf. Table XVII); or rather, the melting-points fall on to two curves—the one for glycerides of acids with an even number of carbon atoms and the other representing the odd series.

The existence of similar triple polymorphism was also established in the case of the  $\alpha$ -mono-

glycerides (T. Malkin *et al.*, J.C.S. 1936, 1628; cf. Fischer, Bergmann and Bärwind, Ber. 1920, **53** [B], 1591; Rewadikar and Watson, J. Indian Inst. Sci. 1930, **13A**, 128) and among the simple  $aa'$ -diglycerides up to  $aa'$ -dipentadecoin: in the case of dipalmitin and higher glycerides, only two modifications of each glyceride could be found (Malkin *et al.*, J.C.S. 1937, 1409). The transitions between the various forms of the diglycerides is more rapid, however, than in the case of the triglycerides.

Since the natural fats are composed of mixtures of several individual glycerides, the phenomenon of the double- or triple-melting-point is liable to be obscured: in some cases, however, such as that of cacao butter, which consists of a relatively small number of component glycerides, the behaviour on melting and solidifying resembles that of a single glyceride. In all cases, however, if it is desired to ascertain the melting-point of a fat which has recently been fused, it is necessary to allow the sample to stand for at least 24 hours (and preferably longer) before making the test.

The chemical formulae and melting-points of a number of synthetic simple triglycerides, of mixed triglycerides which occur commonly in natural fats and of some triglycerides which have been isolated from hydrogenated oils are shown in Table XVIII (figures drawn from the data of many authors collated by Hilditch in Hefter-Schonfeld, "Chemie u. Technologie der Fette u. Fettprodukte," 1936, Vol. I, p. 197, where the original references are quoted: melting-point data, details of preparation, etc., of many monoglycerides, diglycerides and synthetic mixed triglycerides together with the original references are given in this work, also in Lewkowitsch's "Chemistry and Technology of Oils, Fats and Waxes," and in similar textbooks).

Triacetin is used extensively as a solvent and plasticiser (*v.* ACETIN).

**Glycerol Esters of Inorganic Acids.**—*Glyceryl Chlorohydrins.*—The glyceryl chlorohydrins or chlorides of glycerol are chiefly of interest as intermediate products in the synthesis of glycerol from propylene or allyl alcohol (cf. p. 42), and as the starting point for the older syntheses of glycerides.

$\alpha$ -Monochlorohydrin, an oily liquid, b.p. 227°/760 mm. (Berthelot), 159°/100 mm., 139°/18 mm. (Hanriot), 121.5–122.5°/15 mm. (Nivière);  $d_4^{20}$  1.338 (Hanriot),  $d_4^{20}$  1.3215 (Smith, Z. physikal. Chem. 1918, **92**, 717), is miscible in all proportions with water, alcohol or ether: it is formed, together with minor amounts of the  $\beta$ -isomer, when glycerol is heated at 100°C. with moderate amounts of hydrogen chloride (Berthelot, Ann. Chim. Phys. 1854, [iii], **41**, 296; Nivière, Bull. Soc. chim. 1913, [iv], **13**, 893; Compt. rend. 1913, **156**, 1628; Hanriot, Ann. Chim. Phys. 1879, [v], **17**, 62, 67; Conant and Quayle, Organic Syntheses, 1932, Coll. Vol. I, p. 288).

With excess of hydrogen chloride—for example, by treating glycerol with hydrogen chloride in the presence of glacial acetic acid— $aa'$ -dichlorohydrin, b.p. 70–73°/14 mm. is obtained (Conant and Quayle, *op. cit.*, p. 286).

TABLE XVIII.

Glyceride. <sup>1</sup>	Formula. <sup>2</sup>	M. P. °C.	Isolated from. <sup>3</sup>
<i>Simple triglycerides.</i>			
Tri-laurin . . . . .	$C_3H_5(O\cdot OC_{12}H_{23})_3$	45-6	Laurel oil.
Tri-myristin . . . . .	$C_3H_5(O\cdot OC_{14}H_{27})_3$	56-2	Nutmeg butter.
Tri-palmitin . . . . .	$C_3H_5(O\cdot OC_{16}H_{31})_3$	61-5	Palm oil.
Tri-stearin . . . . .	$C_3H_5(O\cdot OC_{18}H_{35})_3$	70-72	Beef-fat; Borneo tallow (traces), cacao butter (traces).
Tri-olein . . . . .	$C_3H_5(O\cdot OC_{18}H_{33})_3$	liquid	Goose-fat.
<i>Mixed triglycerides.</i>			
Di-palmito-stearin . . . . .	$C_3H_5(O\cdot OC_{16}H_{31})_2(O\cdot OC_{18}H_{35})$	55	Cocount oil (traces).
Di-palmito-α-stearin . . . . .	" " " " "	57-5	Goose-fat, mutton-fat.
Di-palmito-β-stearin . . . . .	" " " " "	63	" "
α-Palmito-di-stearin . . . . .	$C_3H_5(O\cdot OC_{16}H_{31})(O\cdot OC_{18}H_{35})_2$	63-3	" "
β-Palmito-di-stearin . . . . .	" " " " "	68	Lard, cacao butter.
Palmito-di-olein . . . . .	$C_3H_5(O\cdot OC_{16}H_{31})(O\cdot OC_{18}H_{33})_2$	liquid	Lard, goose-fat.
Palmito-di-palmitin . . . . .	$C_3H_5(O\cdot OC_{18}H_{33})(O\cdot OC_{16}H_{31})_2$	33-5	Goose-fat.
oleo-di-palmitin . . . . .	" " " " "	38	Cacao butter.
oleo-di-stearin . . . . .	$C_3H_5(O\cdot OC_{18}H_{33})(O\cdot OC_{16}H_{31})_2$	42	Lard.
β-oleo-di-stearin . . . . .	" " " " "	44-5	Cacao butter.
Stearo-di-olein . . . . .	$C_3H_5(O\cdot OC_{18}H_{33})(O\cdot OC_{16}H_{31})_2$	45-46	Seed-fat of <i>Allandlackia Stuhlmannii</i> .
oleo-palmito-stearin . . . . .	$C_3H_5(O\cdot OC_{18}H_{33})(O\cdot OC_{16}H_{31})(O\cdot OC_{18}H_{35})$	liquid	Goose-fat.
" " " " "	" " " " "	31-4	Cacao butter.
oleo-palmito-linolin . . . . .	$C_3H_5(O\cdot OC_{18}H_{33})(O\cdot OC_{16}H_{31})(O\cdot OC_{15}H_{31})$	41	Lard.
<i>Glycerides from hydrogenated oils.</i>			
Myristo-palmito-arachin . . . . .	$C_3H_5(O\cdot OC_{14}H_{27})(O\cdot OC_{16}H_{31})(O\cdot OC_{20}H_{39})$	49-5	Hydrogenated whale oil.
Palmito-stearo-arachin . . . . .	$C_3H_5(O\cdot OC_{16}H_{31})(O\cdot OC_{18}H_{35})(O\cdot OC_{20}H_{39})$	57-3	" "
Di-stearo-arachin . . . . .	$C_3H_5(O\cdot OC_{18}H_{35})_2(O\cdot OC_{20}H_{39})$	62-3	" "
Stearo-di-behenin . . . . .	$C_3H_5(O\cdot OC_{18}H_{35})(O\cdot OC_{22}H_{43})$	?	Hydrogenated rape oil.
Dihydrochaulmoogra-di-dihydrohydrocarpin . . . . .	$C_3H_5(O\cdot OC_{19}H_{33})(O\cdot OC_{16}H_{29})_2$	30-7	Hydrogenated chaulmoogra oil.
Dihydrohydrocarpo-di-dihydrochaulmoogrin . . . . .	$C_3H_5(O\cdot OC_{16}H_{29})(O\cdot OC_{18}H_{33})_2$	42-2	" "

<sup>1</sup> Hyphens have been inserted in the names of the glycerides to facilitate reading, although they are commonly omitted in the literature.

<sup>2</sup> The order in which the acid radicals are formulated merely follows the order used in naming the glycerides: it is not intended to give any indication of their configuration in the glyceride molecule.

<sup>3</sup> Most of the glycerides occur in many different fats: the source mentioned is merely one such, from which the glyceride has been isolated and studied by the investigator.

*β*-Monochlorohydrin, b.p. 146°/18 mm., *d*<sub>4</sub><sup>20</sup> 1.328 (Hanriot, *l.c.*, p. 68) can be prepared by the action of hypochlorous acid upon allyl alcohol, whilst *αβ*-dichlorohydrin, b.p. 182°, is obtained by treating allyl alcohol with chlorine.

Trichlorohydrin (glyceryl trichloride, propenyl trichloride), b.p. 158°, is produced by the action of phosphorus pentachloride upon dichlorohydrin.

The bromo- and iodo-hydrins may be prepared by analogous methods, using the appropriate halogen or halogen acid (for the synthesis of glyceryl-*αα'*-dibromohydrin, b.p. 110–112°/20 mm., *cf.* G. Braun, *Organic Syntheses*, 1934, 14, 42).

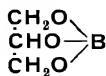
Data concerning a number of derivatives of the chlorohydrins containing fatty acid radicals, such as chlorodilaurin and chlorodistearin, which have been prepared by Grun and others in the course of their work on the synthesis of glycerides, are collated by J. Lewkowitsch in "Oils, Fats and Waxes," 6th ed. Vol. I, ch. 3.

The sulphuric acid esters of glycerol are obtained by dissolving glycerol in concentrated sulphuric acid. On heating with steam, the esters are easily dissociated into glycerol and sulphuric acid. All three possible glycerol sulphuric acids, glyceroltrisulphuric acid, glyceroldisulphuric acid and glycerolmonosulphuric acid are known.

Nitric acid esters of glycerol.—Nitroglycerin (*v. Explosives*, Vol. IV, 491).

Glyceryl arsenite is formed by dissolving arsenious oxide in glycerol and heating to 250°. Above 250° it decomposes. It is volatile with the vapours of glycerol, hence, when distilling the arsenite in a current of superheated steam it is either volatilised unchanged, or is hydrolysed by the steam so that the distillate contains arsenious acid. Glyceryl arsenite is used in calico printing.

Glyceryl borate.—When glycerol is heated to 160° with boric anhydride a yellow hygroscopic mass of glyceryl borate



is obtained; this ester is unstable and is decomposed by water but is somewhat soluble in alcohol (W. R. Dunstan, *Pharm. J.* 1884, 14, 41).

Glyceryl phosphoric esters are obtained by heating phosphoric acid with glycerol. The most important ester, commercially, is monoglycerylphosphoric acid,  $\text{C}_3\text{H}_5(\text{OH})_2\text{O}\cdot\text{PO}(\text{OH})_2$ , which forms a series of salts (sodium, lithium, calcium, strontium, iron, etc.), largely used in pharmaceutical practice (especially in France).

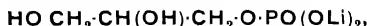
It has been found by Umney and Bennett (*Proc. Brit. Pharm. Conf.* 1914, 22) that the composition of commercial calcium glycerophosphate varies. It should contain at least 15% of calcium, and may contain added citric acid to increase the solubility. The magnesium salt should contain not less than 10% of magnesium, and the ferric salt at least 15% of iron, and be soluble in 2 parts of water. Sodium glycerophosphate crystallises with 5 mol. of water.

The synthetic glycerylphosphoric acid is optically inactive and consists of a mixture of glyceryl-*α*-monophosphoric acid with some glyceryl-*β*-monophosphoric acid: it is not, however, identical with fully racemised "natural glycerylphosphoric acid" which may be recovered from phosphatides of animal or vegetable origin. It has been shown by King and Pyman (*J.C.S.* 1914, 105, 1238) that the commercial crystallised sodium salt introduced by Poulenc Frères (*cf.* F.P. 373112) consisted of sodium glyceryl-*β*-monophosphate. Natural glycerylphosphoric acid consists of a mixture of about 3 parts of the *β*-acid with 1 part of the *α*-isomer, and displays a certain degree of optical activity (*cf.* Karrer *et al.*, *Helv. Chim. Acta.* 1926, 9, 3).

Both glyceryl-monophosphoric acids have been prepared by Karrer *et al.* (*l.c.*) from natural lecithin. The *β*-acid can be precipitated as a crystalline insoluble double salt with barium nitrate. The *α*-acid forms only a simple barium salt, which is precipitated from solution on boiling.

Both glyceryl-*α*-monophosphoric acid and glyceryl-*β*-monophosphoric acid have been synthesised by King and Pyman (*l.c.*; *cf.* Hill and Pyman, *J.C.S.* 1929, 2236), the respective quinine salts melted at 153–154°C. (*cf.* m.p. 155° recorded by Karrer and Benz, *Helv. Chim. Acta.* 1926, 9, 23) and 178–180°C. Glyceryl-*α*-monophosphoric acid has also been synthesised by Karrer and resolved into its optical isomers through the strychnine salt (Karrer and Benz, *l.c.*, and *ibid.* 598).

Optically active glycerylphosphoric acid may be synthesised by adding phosphoryl chloride to a solution of *d*-*α*-bromohydrin in dry pyridine at below –10°. The bromine is removed by lithium hydroxide and the product is isolated as nearly pure lithium *d*-glyceryl-*α*-phosphate



$[\alpha]_D^{18} + 3.51^\circ$  in aqueous solution. Lithium *L*-glycerylphosphate has  $[\alpha]_D^{18} - 3.02^\circ$  (Abderhalden and Eichwald, *Ber.* 1918, 51, 1308).

*L*-(-)-glyceryl-*α*-monophosphoric acid synthesised from *d*(+)-acetone-glycerol by H. O. L. Fischer and Baer (*Naturwiss.* 1937, 25, 589, Baer and H. O. L. Fischer, *J. Biol. Chem.* 1939, 128, 491) is stated to be identical with the natural product obtained from lecithin.

Phosphatides.—Very great physiological interest, as well as some commercial utility, attaches to a group of mixed triglycerides which contain both fatty acid and phosphoric acid residues, and are known as *phosphatides* (Thudichum), *phospholipins* (Leathes) or *phospho-amino lipids*.

Although their precise rôle is not yet fully understood, it is clear that the phosphatides play an extremely important part in the fat-metabolism of the living organism.

In these compounds, two long-chain fatty acid radicals (which may be saturated or unsaturated, *e.g.* stearyl or oleyl residues) and one phosphoric acid residue are combined with glycerol: further, one of the two remaining free hydroxyl groups of the phosphoric acid nucleus is combined with

an organic base—choline in the case of the *lecithin* group of phosphatides, and colamine ( $\beta$ -aminoethanol,  $\beta$ -hydroxyethylamine) in the case of the *kephalins*. The phosphatides, which are described more fully elsewhere (cf. H. and I. S. MacLean, "Lecithin and Allied Substances:—The Lipins," London, 1927; Thierfelder and Klenk, "Chemie der Cerebroside u. Phosphatide," Berlin, 1930; Leathes and Raper, "The Fats," London, 1925), are found widely distributed in small quantities in animal and vegetable tissues (frequently in association with fats), and especially in the physiologically active organs and secretions such as the brain, liver, blood, egg-yolk, milk, etc. They occur in smaller quantities in plant tissues, notably in the seeds of the soya bean.

For the separation of  $\alpha$ - and  $\beta$ -lecithins and -kephalins from soya bean and brain phosphatides, cf. B. Suzuki and collaborators (Y. Yokoyama *et al.*), Proc. Imp. Acad. Tokyo, 1930, **6**, 341; 1931, **7**, 12, 226; 1932, **8**, 183, 358, 361, 424, 428, 490).

Bodies of the lecithin and kephalin type containing saturated fatty acids have been synthesised by Grun and Lampächer (Ber. 1926, **59** [B], 1350; 1927, **60** [B], 147; cf. Hundeshagen, J. pr. Chem. 1883, [ii], **28**, 219): the configuration of these products is discussed by Verkade and Van der Lee (Proc. K. Akad. Wetensch. Amsterdam, 1937, **40**, 858; Fette u. Seifen, 1938, **45**, 457) and by Kabashima and Suzuki (Proc. Imp. Acad. Tokyo, 1932, **8**, 492; Kabashima, Ber. 1938, **71** [B], 76, 1071). Phosphatides containing oleic and other unsaturated acids have been synthesised by Grun and Memmen (unpublished; v. Hefter-Schönfeld, "Chem. u. Technologie d. Fette u. Fettprodukte," 1936, Vol. I, 483; method patented by Hoffmann-La Roche & Co., A.-G., G.P. 608074). For the synthesis of chaulmoogryl and hydno-carpyl glycerophosphatides, see Wagner-Jauregg and Arnold, Ber. 1937, **70** [B], 1459; Arnold, *ibid.* 1938, **71** [B], 1505.

The new methods of Verkade and his collaborators for the synthesis of glycerides (see *above*) may also be adapted for the synthesis of glycerophosphoric acids and phosphatides of known configuration.

The phosphatides are soluble in fats but differ from these in being soluble in alcohol and insoluble in acetone: they emulsify readily with water, and hence find extensive commercial use as emulsifiers in the manufacture of margarine and other technical emulsions, as additions to soap and as a viscosity-modifying agent in the manufacture of chocolate (v. Vol. III, 87c). Lecithin recovered from soya beans now largely replaces lecithin prepared from animal sources (egg-yolk, brains) for commercial purposes.

**Glycerol Ethers.**—Mono- and di-alkyl (or aryl) ethers may be prepared by treating the corresponding chlorohydrins with the appropriate alcohol and caustic soda. The tri-ethers are made from the di-alkyl derivatives by reaction with sodium and an alkyl sulphate.

These ethers are stable, inodorous compounds, possessing excellent solvent properties for organic substances, such as nitrocellulose, resins, oils, etc. The following belong to the class

of "high boiling" or "medium boiling" solvents: monomethyl ether, b.p. 196°; dimethyl ether, b.p. 169°; trimethyl ether, b.p. 148°; monoethyl ether, b.p. 230°; diethyl ether, b.p. 191°; triethyl ether, b.p. 230°; di-isopropyl ether, b.p. 112°; di-isobutyl ether, b.p. 270°. The properties of a number of glyceryl ethers (and also of some glyceryl acetals and ketals) are listed by Du Puis, Lenth and Segor in Oil and Soap, 1941, **18**, 31.

Some, e.g. the *diethyl ether*, are used as lacquer solvents, and others, e.g. the mixed *ditolyl ethers* (b.p. 200–210°/20 mm. in steam), as plasticisers (cf. Fairbourn, Chem. and Ind. 1930, **49**, 1021). The lower members of this series are water-soluble. For the configuration of the isomeric glyceryl ethers, see Fairbourn (J.C.S. 1930 *et seq.*); Hibbert (J. Amer. Chem. Soc. 1928 *et seq.*).

The  $\alpha\beta$ -isopropylidene ether of glycerol ("acetone-glycerol") and the  $\alpha\beta$ - and  $\alpha\alpha'$ -benzylidene ethers are of interest in connection with the synthesis of artificial glycerides (see p. 66a).

**Polyglycerols; Diglycerin.**—*Diglycerin* (Diglycerol ether, diglyceryl alcohol, bis(hydroxypropyl)oxide (Nef, Annalen, 1904, **335**, 239),  $(\text{HO})_2\text{C}_3\text{H}_5-\text{O}-\text{C}_3\text{H}_5(\text{OH})_2$ , is the lowest member of a series of condensation products—ethers—of glycerol which are formed when glycerol is heated. It is present in, and may be separated from, the *glycerin foots* or still residues obtained in the distillation of glycerin. In ordinary circumstances, however, it is more convenient to manufacture diglycerin and polyglycerols by the condensation of pure glycerin (cf. Claessen, G.P. 181754, 198768; Nobel Explosives Co. *et al.*, B.P. 24608/1910; Lever Bros. Ltd., B.P. 442950; U.S.P. 2071459; Henkel & Cie, G.P. 494430; I.G. Farbenind. A.-G., G.P. 575911, 623482). The condensation of glycerin by heating it in the presence of magnesia or silica is claimed to furnish a product consisting largely of diglycerin. Iodine has been used as catalyst for the condensation of glycerin (cf. Claessen, G.P. 181754, 198768; Nobel Explosives Co. *et al.*, B.P. 24608/1910; Lever Bros. Ltd., B.P. 442950; U.S.P. 2071459; Henkel & Cie, G.P. 494430; I.G. Farbenind. A.-G., G.P. 575911, 623482). The condensation of glycerin by heating it in the presence of magnesia or silica is claimed to furnish a product consisting largely of diglycerin. Iodine has been used as catalyst for the condensation of glycerin (cf. Claessen, G.P. 181754, 198768; Nobel Explosives Co. *et al.*, B.P. 24608/1910; Lever Bros. Ltd., B.P. 442950; U.S.P. 2071459; Henkel & Cie, G.P. 494430; I.G. Farbenind. A.-G., G.P. 575911, 623482). The condensation of glycerin by heating it in the presence of magnesia or silica is claimed to furnish a product consisting largely of diglycerin. Iodine has been used as catalyst for the condensation of glycerin (cf. Claessen, G.P. 181754, 198768; Nobel Explosives Co. *et al.*, B.P. 24608/1910; Lever Bros. Ltd., B.P. 442950; U.S.P. 2071459; Henkel & Cie, G.P. 494430; I.G. Farbenind. A.-G., G.P. 575911, 623482).

Lourenço (Ann. Chim. Phys. 1863, [iii], **67**, 299) prepared both diglycerin and triglycerin,  $(\text{C}_9\text{H}_{20}\text{O}_7)$ , b.p. 275–285°/10 mm., by heating glycerol with monochlorohydrin.

*Diglycerin* is an extremely viscous, hygroscopic liquid, b.p. 257–260°C./30 mm. (Lewis), 261–262°C./27 mm. (Nef, *l.c.*); 235–240°C./6 mm. (Nivière, Compt. rend. 1913, **156**, 1776),  $d_{20}^{20}$  1.3215;  $d_{30}^{30}$  1.3183 (Lewis).

**Polyglycerols.**—As the temperature of the condensation of glycerin is increased, "polyglycerols" of higher molecular weight are formed. Thus Rangier (Chim. et. Ind. 1929, Spec. No. 8e (Strasbourg and Luxembourg, Congr. de Chim. ind., (1928), p. 535C) has isolated tri- (cf. Lourenço, *l.c.*), tetra-, penta- and hepta-polyglycerols together with other unidentified solid condensation derivatives, from the products of the polymerisation of glycerol at 245–265°C. in the presence of sodium acetate. Rangier (*l.c.*) suggests that condensation products of the

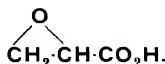
glycide type (*i.e.* in which water has been eliminated between adjacent hydroxyl groups of the same glycerol nucleus) may be formed as well as the ether-type of condensation derivative.

Apart from the older use of glycerin foots in the manufacture of shoe-blackings, hectograph mass, etc., applications of polyglycerols or their esters (including esters of fatty acids and of rosin acids) as lathering and detergent agents, or as assistants in the drawing of threads of cellulose derivatives have been proposed in various patents.

For methods of analysis of mixtures of diglycerol and glycerin, *cf.* Rayner (*l.c.*), Lewis (*l.c.*), Lawrie (*op. cit.*, p. 303).

E. L. and H. E. C.

### GLYCIDIC ACID,



dl-Glycidic acid is prepared by the action of alcoholic KOH on the mixture of *d*-chlorhydracrylic acid and  $\beta$ -chlorlactic acid obtained by treating acrylic acid with hypochlorous acid (Melikow, Ber. 1880, 13, 458; *cf.* Freudenberg, *ibid.* 1914, 47, 2034). It is a liquid miscible in all proportions with water, alcohol and ether. The free acid and its salts readily pass into glyceric acid on warming with water. The ammonium, sodium, potassium and silver salts are crystalline, the calcium and zinc salts are amorphous.

The ethyl ester is insoluble in water and has b.p. 161–163°,  $d_4^{21.6}$  1.0933 (Melikow and Zelinsky, *ibid.* 1888, 21, 2052).

d-Glycidic acid: the potassium salt is prepared by the action of alcoholic KOH on *l*- $\beta$ -bromolactic acid and has  $[\alpha]_D^{18} + 30.2^\circ$ . l-Glycidic acid is similarly prepared from *d*- $\beta$ -bromolactic acid and has  $[\alpha]_D^{18} - 11.7^\circ$  (Abderhalden and Eichwald, *ibid.* 1915, 48, 116).

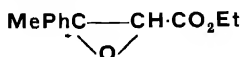
Substituted glycidic acids are obtained from  $\alpha\beta$ -unsaturated aldehydes by treatment with alkali and either alkali hypobromite or hydrogen peroxide, *e.g.* phenylglycidic acid from cinnamaldehyde, and methylglycidic acid from crotonaldehyde (Kaufmann, B.P. 335391).

**GLYCIDIC ESTERS.** Of recent years somewhat mysterious bodies appeared on the synthetic-perfume market under the names " $\text{C}_{16}$  aldehyde (strawberry aldehyde)" and " $\text{C}_{20}$  aldehyde (raspberry aldehyde)."

These so-called aldehydes are in fact glycidic esters, either pure or mixed.

The manufacture of these bodies, which are of considerable importance in the flavouring and perfume trades, is described in detail in B.P. 372013/1931, and is effected by condensing, by means of an alkaline condensing agent, a halogen-acetic acid ester with a cyclic aldehyde, or with an open chain ketone or a saturated cyclic ketone.

The typical strawberry compound, ethyl  $\beta$ -phenyl- $\beta$ -methylglycidate,



is prepared by dissolving acetophenone and ethyl chloracetate in benzene or xylene and condensing with sodamide. It is a colourless liquid, b.p. 132–134°/5 mm., and has an agreeable odour resembling that of strawberries.

The three following esters have a raspberry odour: ethyl 4-ethylphenylglycidate, b.p. 155–160°/3 mm.; ethyl 4-methylphenylglycidate, b.p. 145–147°/3–4 mm.; and ethyl 2,4-dimethylphenylglycidate, b.p. 150–155°/3 mm.

The ethyl esters of the di-isopropylphenylglycidic acids have musk or ambergris odours, and many others of the series are used for modifying flavours and odours. For example, ethyl 2,4-di-isopropylphenylglycidate is a liquid, b.p. 175–185°/3 mm., having an ambergris odour.

E. J. P.

### GLYCIDOL (glycide, epihydrin alcohol),



dl-Glycidol.—A yield of 90% is obtained by the action of metallic sodium on glycerol monochlorhydrin dissolved in anhydrous ether. It is a liquid, b.p. 65–66°/2–2.5 mm.,  $d_4^{20}$  1.1143,  $n_D^{20}$  1.4302.

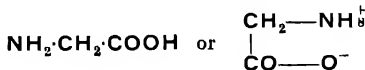
Characteristic derivatives are the phenyl- and  $\alpha$ -naphthyl-urethanes which form colourless needles from high-boiling petroleum and melt at 60° and 102° respectively (Ruder and Hill, J. Amer. Chem. Soc. 1930, 52, 1521).

Ethers.—Methyl, b.p. 115–118°; ethyl, b.p. 124–126°,  $d_4^{20}$  0.9646; isoamyl, b.p. 188°,  $d_4^{20}$  0.90; phenyl, b.p. 243–244°, 133°/23 mm.

l-Glycidol has  $d^{18}$  1.1050 and  $[\alpha]_D^{18} - 8.55^\circ$ .

d-Glycidol has  $d$  1.1054 and  $[\alpha]_D^{18} + 7.69^\circ$  (Abderhalden and Eichwald, Ber. 1915, 48, 1855–1864).

**GLYCINE.** Glycocol, Aminoacetic acid,



(Sakurai, Chem. Soc. Proc. 1894, 90, 1896, 38; Walker, *ibid.* 1894, 94), was discovered in 1820 by Braconnot (Ann. Chim. Phys. 1820, [u], 13, 114) among the products obtained by decomposing glue with sulphuric acid. It is obtained similarly from various proteins (Spiro, Z. physiol. Chem. 1874, 23, 187), and is present as the chief amino-acid in the sugar cane (Shorey, J. Amer. Chem. Soc. 1897, 19, 881; 1898, 20, 137).

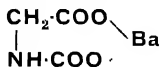
**PREPARATION.**—(1) From chloracetic acid. Chloracetic acid (1 mol.) is dissolved in 4 litres of  $\text{NH}_4\text{OH}$  (sp.gr. 0.90) and allowed to stand for 24 hours at 30° or 2 days at 20° and the excess  $\text{NH}_3$  recovered by distillation. The glycine solution is evaporated to 500 c.c. and 1 mol. of pure silver oxide stirred in until the reaction is over. The filtrate from AgCl is concentrated to 200 c.c., boiled to decompose any silver-ammonia complex, and again filtered. The glycine solution is treated with "norit" (1–2 g.) filtered and treated with an equal volume of 95% EtOH and after 1 hour at 0° filtered; the separated glycine is washed with 95% EtOH

and the crystals dried in a desiccator. Yield, 43 g. (63% containing 0.1 mol. % of  $\text{NH}_4\text{Cl}$ ). To purify—dissolve the product in 200 c.c. water and shake with 10 g. granular "permutite" (after Folin), filter and precipitate the glycine with 250 c.c. 95%  $\text{EtOH}$ . Wash and dry as above. Yield, 37.5 g., 50% on whole process. It is free from  $\text{NH}_3$  and  $\text{Cl}^-$  (Robertson, *ibid.* 1927, **49**, 2889; see also Boutwell and Knick, *ibid.* 1930, **52**, 4166; Orten and Hill, *ibid.* 1931, **53**, 2797; Krause, Chem.-Ztg. 1931, **55**, 666; Kulikov *et al.*, J. Gen. Chem. U.S.S.R., 1932, **2**, 730, 777; Contardi and Ravazzoni, Rend. Ist. Lomb. Sci. Lett. 1933, [ii], **66**, 786; G.P. 616412).

(1) From *Aminoacetonitrile*.—Aminoacetonitrile hydrogen sulphate is hydrolysed with 40%  $\text{H}_2\text{SO}_4$  for 3 hours at  $125^\circ$ . The yield may be >92%. The purification suggested is: heat the glycine solution by superheated steam with enough pure  $\text{BaCO}_3$  to neutralise all acids and expel all  $\text{NH}_3$ . Precipitate the barium as  $\text{BaSO}_4$ . Treat the filtrate with pure  $\text{PbCO}_3$  until neutral, and if  $\text{Cl}^-$  is present, cool to  $0^\circ$  for about 12 hours. Filter and decompose with  $\text{H}_2\text{S}$ . Concentrate the glycine solution and wash the product in  $\text{MeOH}$  (Cocker and Lapworth, J.C.S. 1931, 1391; see also Anslow and King, *ibid.* 1929, 2465).

Glycine can also be obtained by passing cyanogen into boiling hydrochloric acid (sp.gr. 1.06) (Emmerling, Ber. 1873, **6**, 1351); by heating potassium phthalimide with ethyl chloracetate (Gabriel and Kroschberg, *ibid.* 1889, **22**, 427), by treating nitrosomalonic ester with zinc and acetic acid (Conrad and Schulze, *ibid.* 1909, **42**, 729); by boiling hippuric acid with strong sulphuric acid (Curtius, J. pr. Chem. 1882, [ii], **26**, 145; Dessaignes, Annales, 1846, **58**, 322); by treating glyoxylic acid with ammonium carbonate and subsequently heating to  $120^\circ$  with hydrochloric acid (Eilenmeyer, junr. and Kunin, Ber. 1902, **35**, 2438); by the action of hexamethylenetetramine on potassium monochloracetate (Boureet, Bull. Soc. chim. 1898, [iii], **19**, 1005; Auger, *ibid.* 1899, [iii], **21**, 5).

In order to obtain the pure acid, the solution containing the acid, prepared by any of the above methods, is freed from ammonia (if present) and freshly precipitated copper hydroxide is added. The copper salt of the acid which crystallises out is filtered off and decomposed with sulphuretted hydrogen. Another method consists in separating the acid from the impurities present by extraction with glycerol (Farbw. vorm. Meister, Lucius and Bruning, G.P. 141976; Z. angew. Chem. 1903, **16**, 527). Siegfried (G.P. 188005; Chem. Zentr. 1905, I, 1140; 1906, I, 451; 1907, II, 1466) adds barium (or strontium) hydroxide to the ice-cold solution, passes in carbon dioxide, precipitates the barium carbaminoacetate,



by alcohol and decomposes it into glycine and barium carbonate, by heating with water (v. Vol. I, 320d).

**PROPERTIES.**—Glycine crystallises from water in plates and from dilute alcohol in needles (see E. Fischer, Ber. 1905, **38**, 2916; King and Palmer, Biochem. J. 1920, **14**, 582). After drying at  $100^\circ$  the plate form begins to decompose at  $212^\circ$ , whilst the needle form remains unchanged until at  $228^\circ$  it turns brown and at  $232-236^\circ$  melts, turning purple and evolving gas; sp.gr. 1.1607 (Curtius, *l.c.*). It is soluble in 4.3 parts of cold water and in 930 parts of ethyl alcohol (sp.gr. 0.828) but is insoluble in absolute alcohol. Hydriodic acid reduces glycine to ammonia and acetic acid (Kwisda, Monatsh. 1891, **12**, 419), whilst sodium amalgam yields aminoacetaldehyde (Neuberg, Ber. 1908, **41**, 956; E. Fischer, *ibid.* p. 1019). Electrolysis of the acid or the copper salt yields ethylenediamine (Lilienfeld, G.P. 147943; Chem. Zentr. 1904, I, 133; Kuhlmg, Ber. 1905, **38**, 1638; 1907, **40**, 757). Hydrogen peroxide oxidises glycine to glyoxylic acid and formaldehyde (Dakm, J. Biol. Chem. 1905, **1**, 171); treatment with nitrosyl chloride results in the formation of chloroacetic acid (Tilden and Forster, J.C.S. 1895, 191). Glycine and its derivatives are used in photography as developers in place of pyrogallol, etc. (Farbw. vorm. Meister Lucius and Bruning, G.P. 142489; U.S.P. 767815; B.P. 20377/02; J.S.C.I. 1903, **22**, 380). For the biochemistry of glycine, see Nord, Acta. med. Scand. 1926, **65**, 1, Lundin, Biochem. Z. 1929, **207**, 91; Edlbacher and Kraus, Z. physiol. Chem. 1928, **178**, 239; Blix, Skand. Arch. Physiol. 1929, **56**, 131; Christman and Mosier, J. Biol. Chem. 1929, **83**, 11; Re, Rev. Soc. argentina biol. 1929, **5**, 498; Reuter, Z. ges. exp. Med. 1935, **95**, 217.

**DERIVATIVES.**—Aromatic Glycines are prepared from aromatic amines and monohalogenated acetic acids or dihalogenated vinyl ethers (Imbert and Consortium für Elektrochemische Industrie, G.P. 199624). *Glycocollamide* is produced when glycocoll and alcoholic ammonia are heated together at  $160^\circ$ . *Glycocollanilide* is prepared from chlor- or bromoacetanilide and ammonia (Majert, B.P. 5269, 1891, G.P. 59121; J.S.C.I. 1892, **11**, 369).

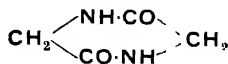
**Esters.**—The *ethyl ester* is prepared by the action of ammonia on chloroacetic acid, and subsequent treatment of the crude dry product with absolute alcohol and dry hydrogen chloride (Hantzsch and Metcalf, Ber. 1896, **29**, 1684; Hantzsch and Silberrad, *ibid.* 1900, **32**, 70) or by the interaction of hexamethylenetetramine and chloroacetic acid and subsequent treatment as above (Auger, Bull. Soc. chim. 1899, [iii], **21**, 5). It boils at  $51.5-52.5/10$  mm. and has  $d_4^{16} 1.0358$  (Schmidt, Ber. 1905, **38**, 200; see also Organic Syntheses, 1934, **14**, 46).

The following esters and their hydrochlorides are described by Abderhalden and Suzuki (Z. physiol. Chem. 1928, **176**, 101): *Propyl*, b.p.  $50-53/16-18$  mm., hydrochloride m.p.  $73-75^\circ$ ; *isopropyl*, b.p.  $52-55/12-15$  mm., hydrochloride m.p.  $84-86^\circ$ ; *butyl*, b.p.  $55-58/8-11$  mm., hydrochloride m.p.  $64-66^\circ$ ; *isobutyl*, b.p.  $60-63/8-11$  mm., hydrochloride m.p.  $70-72^\circ$ ; *n-amyl*, b.p.  $73-76/8-11$  mm., hydrochloride m.p.  $118-120^\circ$ ; *isoamyl*, b.p.  $78-80/8-10$  mm.; and *benzyl*, b.p.  $93-95/8-11$  mm., hydrochloride m.p.  $126-128^\circ$ .



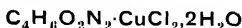
**Glycocolaminocarboxylic Acid Esters** (Einhorn, Chem. Zentr. 1901, 1, 1115; G.P. 108027).

**Glycine anhydride, diketopiperazine,**



discovered by Curtius and Goebel (J. pr. Chem. 1888, [ii], 37, 173). It separates from an aqueous solution of glycine ester on long standing, but is best prepared by treating the hydrochloride of the ester with caustic soda (Fischer, Ber. 1906, 39, 2893). It is a white crystalline solid which, on heating, becomes brown at 245° and melts at 275°.

It forms the compound



with  $\text{CuCl}_2$ , light blue rhombic needles.  $\text{CuBr}_2$  forms the corresponding bromide, bright green monoclinic prisms (Asahina and Dôno, Bull. Chem. Soc. Japan, 1928, 3, 151).

Two molecules each of glycine anhydride and silver nitrate combine to form scaly lustrous crystals, in 80% yield (Asahina, Z. physiol. Chem. 1928, 179, 83; see also Dôno and Asahina, *ibid.* 1929, 186, 133; and for  $\text{FeCl}_3$  Dubský, Vitu and Langer, Metallborse, 1932, 22, 1533).

**Acetaminoacetic acid**, forms colourless, compact, rhombic prisms, m.p. 206–207°, decomp. (Chattaway, J. C.S. 1931, 2495).

**Heptanolmercuric glycocolate**, forms crystals, m.p. 210°, decomposed by  $\text{HCl}$ . It is very toxic and has no diuretic effect (Lévy, Kayser and Sfrus, Bull. Sci. pharmacol. 1931, 38, 573).

**Ethyl aminoacetate glucoside**, melts at 112° and is soluble in but decomposed by water. It has a bitter taste (H. von Euler and Zeile, Annalen, 1931, 487, 163).

**$\alpha$ -Monoglycylglyceride**, m.p. 167–170°, decomposing at 250° (Weizmann and Haskelberg, Compt. rend. 1929, 189, 104).

The following therapeutic compounds are described by Chemische Fabriken J. Wiernik & Co., A.-G.:

(i) **Benzyl diethylaminoacetate hydrochloride**. The ester has b.p. 149–150°/12 mm., and is a strongly basic oily liquid. The crystalline hydrochloride is very soluble in water and begins to melt at 89° (G.P. 537450).

(ii) **Benzyl dimethylaminoacetate hydrochloride**, the ester boils at 138°/18 mm.; the hydrochloride melts at 116° (G.P. 537450).

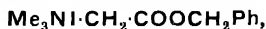
(iii) **Benzyl trimethylaminoacetate hydrochloride**, has m.p. 66–67° and is very soluble in water (G.P. 543556).

(iv) **Benzyl triethanolaminoacetate hydrochloride**,



m.p. 165° (G.P. 543556).

(v) **Benzyl trimethylaminoacetate hydriodide**.



is made by the action of  $\text{CH}_3\text{I}$  on benzyl dimethylaminoacetate, and has m.p. 136–138° (G.P. 556883).

Glycine reacts with phenols forming dyes, giving a blue dyestuff with phenol. A dye is also formed if glycine is treated with 40 c.c. of 25% thymol and 20 c.c. of 5%  $\text{NH}_4\text{Cl}$  solution and bromine added until a red colour appears, followed by  $\text{NaOH}$  until the red colour is just discharged (Fürth and Gotzl, Biochem. Z. 1936, 283, 358).

**Tests for Glycine** are described by Denigès, Bull. Soc. pharm. Bordeaux, 1935, 73, 161, 168; Sánchez, Semana Med. (Buenos Aires), 1930, 37, 1287; Pfeiffer and collaborators, J. pr. Chem. 1930, [ii], 126, 97.

**"GLYCOBROM."** Glyceryl dibromhydrocinnamate.

**GLYCOCHOLIC ACID** (v. Vol. I, 689c).

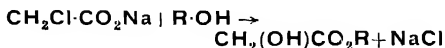
**GLYCOCYAMINE**. Guanidoacetic acid,  $\text{NH}_2\text{C}(\text{NH}_2)\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

**GLYCOGEN** (v. Vol. II, 302d).

**GLYCOGENASE** (v. Vol. V, 14c).

**GLYCOLLIC ACID**, hydroxyacetic acid,  $\text{CH}_2(\text{OH})\text{CO}_2\text{H}$ , is present in sugar cane juice (75–78% of the total acidity), in unripe grapes and in wool wash water. It is formed by the action of alkali on glyoxal, of potassium cyanide on formaldehyde, or by the oxidation of alcohol, glucose or other sugars, etc. On the small scale it is best prepared from chloroacetic acid by treatment with lime or other alkali (cf. U.S.P. 2028064), but technically electrolytic reduction of oxalic acid (G.P. 194038, 204787; cf. Toja and Ceva, Giorn. Chim. Ind. Appl., 1926, 8, 3) appears to be advantageous. A process of oxidising acetylene with intermediate formation of glyoxal forms another subject of patent claims (U.S.P. 1741394).

Glycolic acid forms needles (from water), m.p. 78–79°, although an unstable modification, m.p. 63°, has been described (Muller, Z. physikal. Chem. 1914, 86, 219; Schaum, Schuching and Klausner, Annalen, 1916, 411, 193). On dehydration it yields the normal acid anhydride, as well as the ether anhydride, diglycolic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and polyoxymethylene. Esters of glycolic acid may be obtained not only by normal methods but also by the interaction of anhydrous alcohols with sodium chloroacetate (B.P. 337609):



Glycolic esters of long-chain aliphatic alcohols are of value in that they combine with sodium thiosulphate to give soap-like compounds.

**GLYCOLYSIS**. DEFINITION.—The term "glycolysis" was originally applied to the process by which sugar contained in blood gradually disappears when blood is allowed to stand under sterile conditions outside the body. This phenomenon was first noted by Claude Bernard and the term "glycolysis" was introduced by Lépine. The disappearance of glucose was ascribed by Stosse, and by Embdon and Kraus (Biochem. Z. 1912, 45, 1) to an enzymic fission of a molecule of the carbohydrate into 2 mol. of lactic acid.

Nowadays the term "glycolysis" is understood to cover a wider field than that involved in the breakdown of glucose in blood. Many

investigations since Lépine's work have shown that the breakdown of carbohydrate into lactic acid is a common characteristic of living cells. The classical investigations of Fletcher and Hopkins in 1907 on lactic acid formation in muscle pointed to the great physiological importance of the processes involved in the formation of lactic acid from carbohydrate. Today it is recognised that many, and probably all, of these processes are linked together in the normal metabolic events of the living cell. Each has its part to play in the cell equilibria even if the conditions are such that lactic acid *per se* makes no actual appearance.

It is usual now to define the term "glycolysis" as the sequence of processes involved in the biological formation of lactic acid from carbohydrate.

There has been a tendency in certain schools of biochemistry to restrict the term "glycolysis" to the processes involved in the formation of lactic acid from polysaccharides, glycogen in particular. "Glucolysis" has been the name given to the phenomenon of glucose breakdown to lactic acid, and "fructolysis" has been applied when the sugar in question has been fructose. The majority of workers at present, however, use the term "glycolysis" in its wider meaning—the biological production of lactic acid from all forms of carbohydrates. Accordingly it will be discussed in this sense in this article.

**RELATION TO FERMENTATION.**—Our present knowledge of glycolytic processes has grown with our knowledge of the processes involved in the alcoholic fermentation of glucose by yeasts. The two phenomena are intimately related, the facts concerning one bearing in great detail on those concerning the other. The reader is referred to the articles on FERMENTATION for a full description of many of the substances and reactions which are important both in glycolysis and fermentation.

**BLOOD GLYCOLYSIS.**—This process, the first example of the biological breakdown of glucose into lactic acid to be investigated, varies in speed in the blood of animals of different species. It is relatively rapid in the blood of dog and slow in that of rabbit. Engelhardt and Ljubimowa (Biochem. Z. 1930, 227, 6) give the following order of glycolytic activities of the bloods of different animals: ox>goat>dog>horse>guinea-pig>man>rabbit (see, however, Bürger (Arch. Exp. Pharm. Path. 1930, 150, 298) who considers the glycolytic activities of the bloods of guinea-pig, man, rabbit and rat to be about the same). The velocity of glycolysis in blood is approximately constant at 37° for the first 2 or 3 hours, about 20 mg. per cent. glucose per hour disappearing in the case of human blood. The velocity of glycolysis falls off more and more sharply after the initial constant period, this being largely due to the development of acid conditions caused by lactic acid liberation. According to Roche and Roche (Compt. rend. Soc. Biol. 1927, 96, 361) a decrease in blood  $p_H$  of 0.5 diminishes the rate of glycolysis by 30–40%; it ceases at  $p_H$  5.5 and is optimal at  $p_H$  8.2. Three hours' glycolysis causes a drop in  $p_H$  of 0.2–0.3. The temperature coefficient of the process is 2.1.

According to Irving (Biochem. J. 1926, 20, 613) blood glycolysis takes place in red blood cells, lysis of which results in a disappearance of the glycolytic process. Apparently, therefore, integrity of the cells is important for the accomplishment of the breakdown of glucose. Glycolysis does not occur in serum or plasma. Red blood cells which have been washed with saline solution (0.9% NaCl) will bring about glycolysis in a glucose-saline solution. Meyerhof (Biochem. Z. 1932, 246, 249) has shown that it is possible to separate a glycolytic system from the red blood cell.

Both leucocytes and erythrocytes contribute to the glycolysis of blood, the former being much more reactive per cell than the latter. Ratios of 100:1 and 1,000:1 have been recorded (Maclean and Weir, Biochem. J. 1925, 9, 412). It has been calculated that 6–35% of the glycolysis of normal blood is due to the leucocytes.

The rate of blood glycolysis, in contrast to that of intact tissues which will be discussed later, is the same whether the reaction takes place in oxygen or nitrogen (Katayama, J. Lab. Clin. Med. 1926, 12, 239). This is to be correlated with the fact that the respiration of red blood cells is practically nil. The rate of aerobic glycolysis of leucocytes which are capable of respiration, is a little less than that of anaerobic glycolysis, but this has been disputed (Bakker, Klin. Woch. 1927, 6, 252). Levine and Meyer (J. Biol. Chem. 1912, 11, 361; 12, 265) found that leucocytes form lactic acid from glucose, mannose and galactose.

The rate of glycolysis in blood is independent of the concentration of glucose when this lies within the limits found in human blood. There is no difference between the rates of glycolysis of the blood of normal and diabetic individuals. Addition or absence of insulin has no influence on the process.

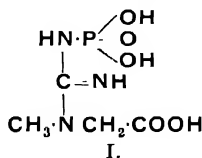
Little is known with certainty of the mechanism of the glycolytic processes in blood. There is evidence to suggest that a phosphorylation takes place (Meyerhof, Biochem. Z. 1932, 246, 249) and the indications are that the processes are similar to those taking place in other tissues.

**GLYCOLYSIS IN MUSCLE.**—According to von Furth (*ibid.* 1915, 69, 199) there are between 350 and 550 mg. lactic acid in 100 g. fresh muscle of man, horse, dog and ox. The lactic acid arises chiefly from breakdown of muscle glycogen. Fletcher and Hopkins (J. Physiol. 1907, 35, 247) showed that lactic acid is formed when frog's muscle contracts in the absence of oxygen but that under aerobic conditions the lactic acid does not accumulate. It was concluded as a result of investigations of Hill and Meyerhof that during the contraction of muscle, glycogen breaks down to lactic acid, the energy liberated being used for the contraction. After relaxation of the muscle, lactic acid is re-synthesised into glycogen, the energy for re-synthesis being supplied by the complete oxidation of a fraction ( $\frac{1}{3}$ ) of the glycogen.

It is known, however, that during the contraction of muscle phosphates make their appearance as well as lactic acid. Addition of phosphates in excess to muscle kept under anaerobic

conditions leads to an increased yield of lactic acid. Hexosediphosphate formed during the fermentation of glucose by yeast, yields lactic acid and free phosphate in the presence of muscle juice, and the addition of this ester to a contracting muscle has much the same effect on the yield of lactic acid as the addition of phosphate and glycogen. These observations led Embden and his colleagues to suggest that the precursor of lactic acid in muscle was a carbohydrate-phosphate complex to which they gave the name *lactacidogen*. They isolated such a substance from the fresh pulp of striated muscle and showed that it yielded an osazone on treatment with phenylhydrazine, identical with that formed from hexosediphosphate prepared by yeast fermentation of glucose. Embden and Zimmermann (*Z. physiol. Chem.* 1924, **141**, 225) prepared the brucine salt of lactacidogen (15 g. of the recrystallised salt from the muscles of one rabbit) and proved it to be the salt of hexosediphosphoric acid. Its physical properties (solubility, optical rotation and melting-point) were identical with the same salt of hexosediphosphoric acid obtained from yeast. It is to be concluded that the same phosphoric acid ester is involved in muscular contraction as in yeast fermentation; that in the former case it is a precursor of lactic acid and in the latter case of alcohol.

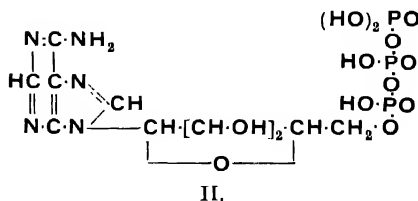
A further phosphoric acid ester important in the sequence of metabolic events in contracting muscle was then discovered (Eggleton and Eggleton, *Biochem. J.* 1927, **21**, 190). This ester is hydrolysed during muscular contraction and is re-synthesised after relaxation; it was proved by Fiske and Subbarow (*Science*, 1926, **65**, 403) to be phosphocreatine (I).



This ester assumed considerable importance when Lundsgaard (*Biochem. Z.* 1930, **227**, 51) discovered that muscle poisoned with iodoacetic acid contracted without lactic acid formation, but with the hydrolysis of phosphocreatine into creatine and free phosphoric acid. It appeared from this discovery that lactic acid as such plays no important part in the contraction of muscle and that its formation depends on subsequent chemical events. Its production, in fact, occurs mainly after relaxation and coincides with the anaerobic re-synthesis of phosphocreatine. Lundsgaard has shown that with muscle poisoned with iodoacetic acid contraction in nitrogen is followed by phosphocreatine breakdown and has put forward the view that the energy of glycolysis (glycogen to lactic acid) is used for the re-synthesis of creatine phosphoric acid at a subsequent stage.

**ADENYLPIROPHOSPHATE.**—The classical discovery in 1906 by Harden and Young of an ultra-filterable and thermostable co-enzyme

essential for the fermentation of glucose by yeast was followed by investigations as to whether muscle glycolysis was equally in need of a co-enzyme. Meyerhof (*Z. physiol. Chem.* 1918, **101**, 165; **102**, 1, 185) showed that a co-enzyme was required for lactic acid formation in muscle and he came to the conclusion it was related to the cozymase of Harden and Young. Work by Euler and Myrback proved that the co-enzyme contained adenine and phosphoric acid and indicated it to be adenylic acid or a derivative of this substance. Lohmann in 1929 isolated from muscle adenylypyrophosphate (II)



and this ester has now assumed the greatest importance in the sequence of events in the cell leading to the formation of lactic acid from carbohydrate.

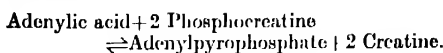
Meyerhof, Lohmann and Meyer (*Biochem. Z.* 1931, **237**, 437) and Lohmann (*ibid.* 1931, **237**, 445) showed that the glycolytic activity of a muscle extract gradually disappears on lengthy standing at 37° or 20° due to autolytic changes and that the activity is restored by the addition to the autolysed extract of minute quantities of adenylypyrophosphate. Autolysis results in the disappearance of this ester which must be restored to regain glycolytic activity. If the extract is dialysed, the loss in activity is not restored by the addition of adenylypyrophosphate alone but the further addition of magnesium ions is essential. The total co-enzyme system consists of adenylypyrophosphate and magnesium ions together also with phosphate ions.

Lohmann (*ibid.* 1931, **241**, 50) further showed that whereas adenylypyrophosphate acted as a co-enzyme for lactic acid formation from glycogen in a dialysed muscle extract, cozymase had no such effect.

It is now recognised that adenylypyrophosphate owes its catalytic influence to its power of transferring phosphate to other molecules in the presence of appropriate enzymes. The adenylic acid system is a phosphorylating-dephosphorylating system for which magnesium ions appear to be indispensable. It is not known whether magnesium ions are required for all phosphorylating processes.

The recognition that adenylypyrophosphate acts as a phosphate donor, adenylic acid being formed with the loss of 2 mol. of phosphoric acid, arose from the discovery that phosphocreatine breakdown in muscle occurs only in the presence of the adenylic acid system (Lohmann, *Naturwiss.* 1934, **22**, 409). Meyerhof and Lohmann (*Biochem. Z.* 1932, **253**, 431) had shown earlier that synthesis of phosphocreatine in muscle takes place at the expense of adenyly-

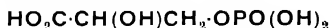
pyrophosphate. The following equilibrium is established :



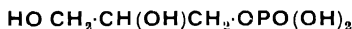
In the presence of a dephosphorylating enzyme in the muscle extract, breaking down adenylpyrophosphate to adenylic acid and free phosphoric acid, the equilibrium above is shifted far to the right.

**PRODUCTS OF CARBOHYDRATE BREAKDOWN IN PRESENCE OF MUSCLE TISSUE.**—It was shown by Lohmann (Biochem. Z. 1930, 222, 324) and by Lipmann and Lohmann (*ibid.* 389) that muscle tissue in the presence of glycogen and of fluoride gives rise to other phosphoric acid esters besides the true Harden-Young hexosediphosphate to which reference has already been made. A fraction of the esters has the same elementary composition as hexosediphosphate but it is more resistant to acid hydrolysis. These resistant "unhydrolysable" esters are also formed when the monophosphoric acid esters of hex- described by Robison, Neuberg and Embden are added to muscle extracts containing fluoride and phosphate ions.

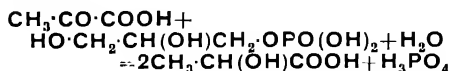
Embden, Denticke and Kraft (Klin. Woch. 1933, 12, 313) showed that a constituent of the "unhydrolysable" ester was phosphoglyceric acid (glyceric acid-monophosphoric acid) which had already been isolated in 1930 by Nilsson in his studies of yeast fermentation of carbohydrate. Another constituent of the "unhydrolysable" ester proved to be *l*- $\alpha$ -glycerophosphoric acid and the acid-resistant ester was found to consist of equimolecular proportions of phosphoglyceric acid and glycerophosphoric acid, *i.e.*



and

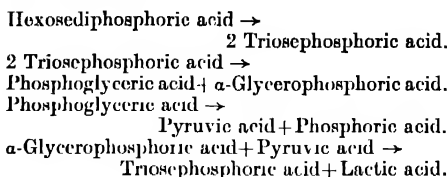


Embden and his colleagues found that phosphoglyceric acid is transformed into pyruvic acid in presence of minced muscle. They showed, moreover, that although the addition of pyruvic acid alone, phosphoglyceric acid alone, or of  $\alpha$ -glycerophosphoric acid alone to muscle extract free from carbohydrate led to no formation of lactic acid, the addition of a mixture of phosphoglyceric acid and of  $\alpha$ -glycerophosphoric acid resulted in the production of lactic acid. Further, the addition of a mixture of pyruvic acid and  $\alpha$ -glycerophosphoric acid to muscle tissue led to lactic acid formation according to the following equation :



The addition of glyceraldehydephosphoric acid (synthesised by Fischer and Baer (Ber. 1932, 65 [B], 337)) to muscle tissue leads to the formation of lactic acid (Embden); and Meyerhof and Kiessling (Biochem. Z. 1933, 264, 40) showed that in muscle extracts one half of the glyceraldehydephosphoric acid (one optical component) is changed into a mixture of phosphoglyceric acid and glycerophosphoric acid. These facts led Embden to the following scheme

for the course of lactic acid formation in a muscle extract :



Meyerhof and McEachern (Biochem. Z. 1933, 260, 417) found that in a muscle extract pyruvic acid was formed from hexosediphosphate or glycogen. On addition of sulphite the yield of pyruvic acid was increased and that of lactic acid decreased. They concluded that pyruvic acid is a normal intermediate in the formation of lactic acid, as required by Embden's scheme. It was recognised independently by Embden and by Meyerhof that the formation of pyruvic acid in muscle must be accompanied by a simultaneous reductive process; this was the formation of  $\alpha$ -glycerophosphoric acid.

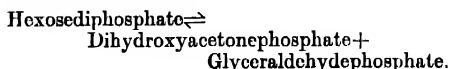
The details of Embden's scheme have been confirmed in Meyerhof's laboratory, where independent work on the same lines was in progress. Meyerhof has developed the scheme to apply to the formation of alcohol from glucose by yeast.

Meyerhof considered at first that the triosephosphate, produced as the initial stage in the breakdown of hexosediphosphate, was glyceraldehydephosphoric acid. He and Lohmann (Naturwiss. 1934, 22, 134) found that the triose-ester formed by the action of dialysed muscle on hexosediphosphate was composed largely of dihydroxyacetonephosphate, and it was shown (Biochem. Z. 1934, 271, 89; 273, 413) that in dialysed muscle extracts an equilibrium mixture of hexosediphosphate and dihydroxyacetonephosphate is rapidly formed from each other. This reaction is controlled by an enzyme *zymohexase* which is not inhibited by fluoride or iodoacetate. The equilibrium obeys the equation

$$\frac{[\text{Dihydroxyacetonephosphate}]^2}{[\text{Hexosediphosphate}]} = K$$

the breakdown of hexosediphosphate being an endothermic reaction. Dihydroxyacetonephosphate has been synthesised by Kiessling (Ber. 1934, 67 [B], 869). It is decomposed quickly by *N*-NaOH at room temperature yielding lactic and phosphoric acids. With *N*-HCl at 100° methylglyoxal and phosphoric acid are formed. Meyerhof and Kiessling (Biochem. Z. 1935, 279, 40) have shown that in dialysed muscle phosphoglyceraldehyde is transformed into dihydroxyacetonephosphate; possibly an equilibrium is established between the two trioses.

According to Meyerhof, Lohmann and Schuster (*ibid.* 1936, 286, 301, 319) there exists in dialysed muscle extracts an enzyme (*aldolase*) bringing about aldol condensation of dihydroxyacetonephosphate with various aldehydes. They suggest that the following equilibrium occurs :



The glyceraldehydephosphate changes subsequently into dihydroxyacetonephosphate.

Two further phosphoryl esters, formed as intermediate substances, have been isolated, viz. phospho(enol)pyruvic acid by Lohmann and Meyerhof (*ibid.* 1934, 273, 60) and 2-phosphoglyceric acid by Meyerhof and Kiessling (*ibid.* 1935, 276, 239). In a dialysed extract of muscle 3-phosphoglyceric acid is converted into 2-phosphoglyceric acid through the agency of an enzyme named *phosphoglyceromutase*, whilst 2-phosphoglyceric acid is converted by an enzyme (*enolase*) into phospho(enol)pyruvic acid. All these esters form equilibrium mixtures (*ibid.* 1935, 280, 99, 100). (For the syntheses of these esters, see Kiessling, *Ber.* 1935, 68 [B], 243, 597.) Sodium fluoride inhibits the breakdown of 2-phosphoglyceric acid.

The decomposition of phosphopyruvic acid into pyruvic acid, which is the immediate precursor of lactic acid, requires the co-operation of a catalyst, viz. adenylypyrophosphate. The participation of this molecule in phosphorylations of carbohydrate and its breakdown products will now be considered.

CATALYTIC INFLUENCE OF THE ADENYLIC ACID SYSTEM IN GLYCOLYSIS.—Meyerhof and Lohmann (*Naturwiss.* 1931, 19, 575) were the first to suggest that the rôle of adenylypyrophosphate as a coenzyme in muscle glycolysis consists in the phosphorylation of carbohydrate, the pyrophosphate breaking down and being re-synthesised at a later period.

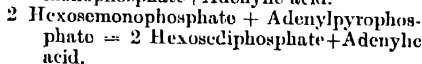
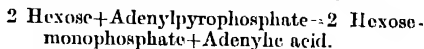
Emhden and Parnas demonstrated that ammonia is formed during muscular contraction, the ammonia arising from the breakdown of adenylic acid by a deaminase yielding also inosmic acid. Muscle deaminase does not attack adenylypyrophosphate, so that evidently the appearance of ammonia is an indication of the appearance of adenylic acid. In presence of a high phosphate concentration ammonia is not formed and this was ascribed to the conversion of adenylic acid into the pyrophosphate (Parnas, Ostern and Mann, *Biochem. Z.* 1934, 272, 64; 1935, 275, 74, 164). It was found by Parnas and his colleagues that the breakdown of glycogen in the presence of phosphates was mainly responsible for the prevention of the appearance of ammonia and for preserving the integrity of the adenylypyrophosphate. If glycogen breakdown was inhibited by iodoacetate or fluoride, ammonia made its appearance. It was shown that the re-synthesis of adenylypyrophosphate was accomplished by breakdown products of glycogen, viz. phosphopyruvic and phosphoglyceric acids. (*See also* Necdham and van Heyningen, *Biochem. J.* 1935, 29, 2040.)

Since adenylypyrophosphate, in muscle pulp poisoned with iodoacetic acid, is not synthesised from adenylic acid and free phosphate ions, and since phosphopyruvic acid or phosphoglyceric acid is essential as a source of phosphate for the synthesis, it follows that phosphate transfer takes place from these acids to adenylic acid. The phenomenon is similar to that already mentioned, which occurs in a muscle extract, between adenylic acid and phosphocreatine. The enzymes responsible for the phosphate transfers from phosphorylated molecules to adenylic

acid have been termed *phosphorylases* (Quastel, *Ann. Rev. Biochem.* 1936, 5, 45).

Lohmann and Meyerhof demonstrated that breakdown of phosphopyruvic acid in a muscle extract only occurs in presence of the adenylic acid system (*Biochem. Z.* 1934, 273, 60).

Phosphorylases appear to be necessary for the phosphorylation of carbohydrate as the first stage in glycolysis, but this is not yet certain. Probably the following reactions take place:

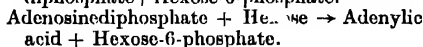
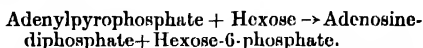


Runnström and colleagues (*ibid.* 1934, 271, 15; *J. Gen. Physiol.* 1935, 18, 717) and Dische (*Biochem. Z.* 1934, 274, 51; 1935, 280, 248) have reported experiments showing that esterification of inorganic phosphate in lysed red blood cells is coupled with the degradation of hexosephosphate. Degradation of glucose or its phosphate is preceded by phosphorylation, the phosphate being derived from adenylypyrophosphate (Dische, *ibid.* 1935, 280, 248). Evidence exists that phosphoric acid can be transferred from hexosephosphates to adenylic acid as well as in the reverse direction (Neuberg, *ibid.* 1935, 280, 163; Lutwak-Mann and Mann, *ibid.* 1935, 281, 140; Ohlmeyer, *ibid.* 1935, 283, 114).

Parnas (*Ergeb. Enzymforsch.* 1937, 6, 57), however, considers that a phosphorylation of glycogen to hexosemonophosphate may occur in the absence of the adenylic acid system. Recent evidence indicates that from glycogen in a muscle extract, glucose-1-phosphoric acid is first formed (Cori and Cori, *Proc. Soc. Exp. Biol. Med.* 1936, 34, 702; 1937, 36, 119). This is known as the *Cori ester*. This ester is rapidly converted into the 6-ester by an enzyme termed *phosphoglucomutase* (Cori, Colowick and Cori, *J. Biol. Chem.* 1938, 124, 543). Cori and his colleagues state that the synthesis of the Cori ester from glycogen in muscle extracts is greatly accelerated by adenylic acid (Cori, Colowick and Cori, *ibid.* 1938, 123, 375, 381). Kendal and Stickland (*Biochem. J.* 1938, 32, 572) find that adenylic acid is essential for the conversion of glycogen into the Cori ester, the reaction being strongly stimulated by magnesium ions.

The conversion of the Cori ester into the 6-ester is also stimulated by magnesium ions. This transformation is followed by the phosphorylation of the 6-ester, via the adenylic acid system, into hexosediphosphate (Harden-Young ester).

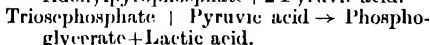
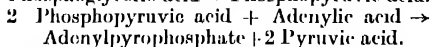
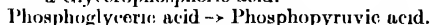
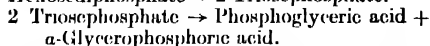
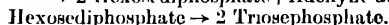
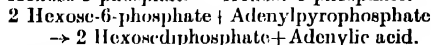
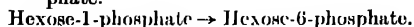
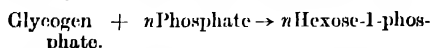
The enzyme, *hexokinase*, discovered by Meyerhof in 1927, catalyses, in the presence of Mg ions, the transfer of phosphate from adenylypyrophosphate to glucose or fructose. The reactions involved are:



The second reaction requires in addition to hexokinase a protein catalyst present in muscle,

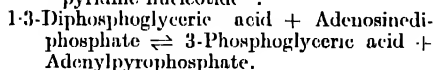
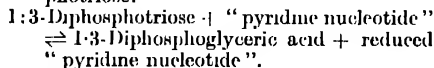
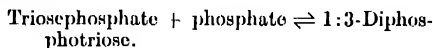
but not in liver or kidney extracts (see Kalkut, Chem. Rev. 1941, 28, 71).

The following equations express the series of reactions in glycolysis and indicate the important position taken by adenylypyrophosphate:

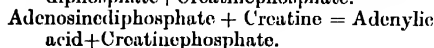


(see also Vol. V, p. 31).

It has lately been shown by Warburg and Christian (Biochem. Z. 1939, 303, 40) that a separation of enzymes involved in glycolytic changes is possible and this has resulted in the demonstration, and isolation, by Negelein and Bromel, of another important intermediate, viz. 1:3-diphosphoglyceric acid. The sequence of enzyme-catalysed reactions are apparently as follows:

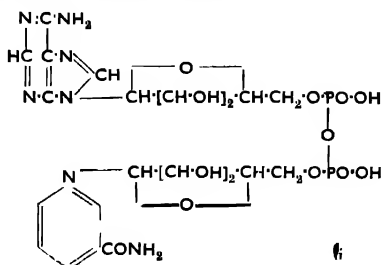


The reaction between adenylypyrophosphate and creatine is important, so far as glycolysis is concerned, in providing a store of phosphate donor in the form of phosphocreatine. It proceeds in two stages:



(Lehmann, *ibid.* 1936, 286, 336).

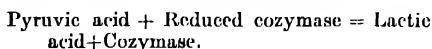
According to Meyerhof, Ohlmeyer and Mohlo (*ibid.* 1938, 297, 90, 113) phosphorylation of adenylic acid may be coupled with oxidative changes and Needham (Enzymologia, 1938, 5, 158) has arrived at a similar conclusion (*cf.* Parnas, *ibid.* 1938, 5, 166 for a recent review of the subject of phosphorylation).



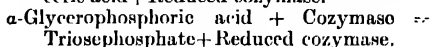
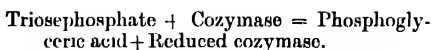
III.

### Part Played by Cozymase in Glycolysis.—

Cozymase plays an important part in muscle glycolysis since it is a necessary carrier in the reduction of pyruvic acid to lactic acid. This molecule is an adenine-nicotinamidedinucleotide III (*n.* Vol. V, p. 15). It acts as a hydrogen carrier, the nicotinic acid amide moiety of the molecule undergoing reduction and oxidation under appropriate conditions. Cozymase is necessary for the activity of lactic acid dehydrogenase and it is this enzyme which activates pyruvic acid as a hydrogen acceptor. Lactic acid is formed according to the equation:



Cozymase is reduced by triosephosphate or by  $\alpha$ -glycerophosphoric acid in presence of their respective dehydrogenases, thus:



Thus the presence of appropriate dehydrogenases in muscle extracts together with that of cozymase enables the necessary hydrogen transfer to take place between triosephosphate and pyruvic acid with lactic acid production. The existence of these dehydrogenases in muscle extract has been established by Adler, Euler and Hughes (Z. physiol. Chem. 1938, 252, 1) and Quastel and Wheatley (Biochem. J. 1938, 32, 936). It was already known from the work of Euler and his colleagues (Z. physiol. Chem. 1937, 245, 217) that cozymase is required for the interaction of triosephosphate and pyruvic acid in a tissue extract.

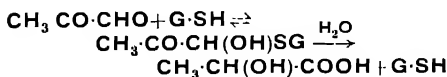
According to Meyerhof, Schulz and Schuster (Biochem. Z. 1937, 293, 309) the reaction between triosephosphate and cozymase only takes place if at the same time there is a transfer of phosphate through adenylypyrophosphate to a suitable phosphate acceptor. (*See also* Needham and Pillai, Biochem. J. 1937, 31, 1837.) The question of coupling between oxido-reductions and phosphorylation processes, particularly that of adenylic acid, is at present under investigation.

How far cozymase is involved in any of the other steps of the glycolytic process is not known with certainty. (*Cf.* Runnström and Michaelis, J. Gen. Physiol. 1935, 18, 717.)

**GLYOXALASE.**—Dakin and Dudley (J. Biol. Chem. 1913, 14, 155, 423; 15, 127) and Neuberg (Biochem. Z. 1913, 49, 502; 51, 484) discovered that methylglyoxal is transformed in tissues into lactic acid, the enzyme responsible being termed by Dakin *glyoxalase*. The rapidity of this transformation gave rise to the view that methylglyoxal might occupy an important position in glycolysis, particularly when considered in relation to Neuberg's conceptions of the course of alcoholic fermentation (*cf.* Neuberg and Oppenheimer, *ibid.* 1925, 166, 450; Neuberg and Gorr, *ibid.* 482). Methylglyoxal was held to arise by loss of water from glyceraldehyde, the latter molecule being formed by fission of the hexose molecule. Neuberg and his colleagues

(1929) isolated methylglyoxal as the 2:4-dinitrophenylhydrazone in almost theoretical yield from specially prepared yeast extracts incubated with hexosediphosphate; the yield was 20–30% of theory with mammalian tissues. Case and Cook (Biochem. J. 1931, 25, 1319) were able to detect both methylglyoxal and pyruvic acid among the products of metabolism. It is, however, uncertain whether the methylglyoxal is a normal product in the course of breakdown of carbohydrate.

The transformation of methylglyoxal into lactic acid by glyoxalase requires the participation of a co-enzyme, which Lohmann found to be glutathione (Biochem. Z. 1932, 254, 332). Jowett and Quastel (Biochem. J. 1933, 27, 486) showed that methylglyoxal combines with glutathione and that it is this compound which breaks down in presence of glyoxalase to form lactic acid and glutathione:



The formulation of the Embden-Meyerhof scheme of glycolysis includes no participation of methylglyoxal. Support for the conclusion that methylglyoxal is not a necessary intermediate in the formation of lactic acid from glycogen comes from Lohmann's observation (Biochem. Z. 1933, 262, 152) that a muscle extract free from glutathione converts glycogen into lactic acid. Moreover, the addition of glutathione brings about no additional glycolysis.

This fact, however, does not necessarily mean that a second route of lactic acid formation from carbohydrate does not take place in the living cell. Support for this dual route of glycolysis *via* methylglyoxal has been found. Investigating lactic acid fermentation by yeast, Auhagen and Auhagen (*ibid.* 1934, 268, 247) find that methylglyoxal is formed and that it is a primary product of reaction and not an artefact. Kobel and Collatz (*ibid.* 1934, 268, 202) conclude that methylglyoxal is formed from sugars. Tissue treated so as to inhibit glyoxalase activity produces methylglyoxal from hexosediphosphate (Neuberg and Simon, Ergen. Enzymforsch. 1933, 2, 118) and from glyceraldehydephosphate (Barronscheen and Beneschovsky, Biochem. Z. 1933, 265, 159). Jowett and Quastel (Biochem. J. 1934, 28, 162) show that glyoxalase activity of intact tissue in presence of low concentrations of methylglyoxal is sufficiently rapid to account for the rate of tissue glycolysis.

It is reasonable to assume that a separate mechanism of glycolysis in addition to that embraced by the Embden-Meyerhof scheme may occur in the intact cell (see also Ashford, *ibid.* 1933, 27, 903).

GLYCOLYSIS IN BRAIN.—Warburg, Posener and Negelein (Biochem. Z. 1924, 152, 309) showed that brain tissue in presence of glucose produces lactic acid with great rapidity *in vitro*. McGinty and Gsell (Amer. J. Physiol. 1925–26, 75, 70) have carried out experiments showing that lactic acid formation in brain takes place at 37° immediately after removal of the brain from the body. The lactic acid was

formed at the rate of 20 mg. per 100 g. tissue per minute. Carbon monoxide anoxemia results in an increase in the amount of lactic acid found in brain after death. Avery, Kerr and Ghantus (J. Biol. Chem. 1935, 110, 637) find that if brain, taken immediately after death of the animal, is frozen in liquid air, the lactic acid content of the brain is initially smaller than was originally supposed. An average value of lactic acid was found to 15.3 mg. per 100 g. cat's brain and 22.3 mg. per 100 g. dog's brain. No significant difference between the lactic acid contents of cerebrum and cerebellum was observed.

Both glycogen and glucose are known to be precursors of brain lactic acid. Kerr (*ibid.* 1938, 123, 443) has isolated 36 mg. glycogen from 100 g. brain tissue, the carbohydrate being identical with liver glycogen. Glucose, however, appears to be the main precursor of brain lactic acid. Holmes and Sherif (Biochem. J. 1932, 26, 381) found that the amount of lactic acid formed on anaerobic incubation of brain depends on the level of blood sugar at the time of death. During insulin hypoglycaemia cerebral lactic acid may amount to only small (e.g. less than half the normal) values. Hyperglycaemia increases brain lactic acid formation. The amount of lactic acid formed is equivalent to the fall in carbohydrate in the brain.

Whereas brain tissue anaerobically *in vitro* (either in the form of thin slices or in a minced condition) breaks down glucose rapidly to lactic acid, it has practically no glycolytic effect on added glycogen. In muscle, on the other hand, the reverse is the case, glycogen breakdown being far more rapid than glucose breakdown to lactic acid (Geiger, *ibid.* 1935, 29, 811; Gaddie and Stewart, *ibid.* 1935, 29, 2101). Probably glyoxalase activity is very much greater in brain than in muscle. Glutathione, the co-enzyme of glyoxalase, has little or no effect on glycogen breakdown in brain or muscle but increases lactic acid production from glucose in brain (Geiger, *loc. cit.*; see, however, Baker, Biochem. J. 1937, 31, 980).

Ashford and Holmes (*ibid.* 1929, 23, 748; 1930, 24, 1119) consider that brain may produce lactic acid in two ways; one, involving glycogen, proceeds through a stage of phosphorylation and another, involving glucose, does not include a phosphorylation stage. The former is quantitatively the less important.

The question, however, as to whether glucose undergoes preliminary phosphorylation in intact brain before further metabolism occurs is still unsettled. Adler and his colleagues (Naturwiss. 1937, 24, 282) have shown that a cell-free product prepared by acetone precipitation of a brain extract is capable of causing glycolysis of glucose so long as adenylic acid, cozymase and a trace of hexosediphosphate are present. This would indicate that phosphorylation of glucose is necessary prior to glycolysis in a brain extract. Geiger (Nature, 1938, 141, 373) states that cytotoxicity of brain releases an inhibitor of glycolysis. By the addition to a brain extract of a factor in muscle extract and of glutathione, creatine phosphate and cozymase a glycolytic breakdown of glucose is obtained the activity of which may be twice that of intact brain.

Such a system also breaks down glycogen, at a smaller rate than glucose, to lactic acid. Phosphate is esterified in brain during glycolysis (see also Geiger, *Biochem. J.* 1940, **34**, 465). According to Cori, Colowick and Cori (*J. Biol. Chem.* 1938, **123**, 375) glucose-1-phosphate is formed from glycogen and inorganic phosphate in dialysed extracts of rabbit brain. The amount is increased by the addition of adenylic acid. The conversion of glucose-1-phosphate into glucose-6-phosphate takes place more slowly than in muscle.

Macfarlane and Weil-Malherbe (*Biochem. J.* 1941, **35**, 1) conclude that brain glycolysis is maintained by a cycle of phosphorus transferences involving 0.1-0.2 mg. P per g. dry brain tissue. They find that during anaerobic glycolysis by rabbit-brain slices the inorganic phosphate is maintained at its initial level whilst the content of pyrophosphate falls to about one-third of the original. Anaerobic incubation without glucose leads to a rapid disappearance of pyrophosphate with a simultaneous loss of glycolytic power. Hexosediphosphate is present in small quantities in glycolysing brain.

**ANAEROBIC GLYCOLYSIS OF TISSUES *IN VITRO***—Warburg and his colleagues have measured the rates of lactic acid formation of thin sections of animal tissues examined in a glucose-Ringer medium under anaerobic conditions. Typical results are recorded in Table I (*Biochem. Z.* 1927, **184**, 484).

TABLE I.

	$Q_M^{N_2}$ *
Kidney (rat) . . . . .	3
Liver . . . . .	3
Intestinal mucosa (rat) . . . . .	4
Spleen (rat) . . . . .	8
Testis (rat) . . . . .	8
Pancreas (rabbit) . . . . .	3
Thymus (rat) . . . . .	8
Brain cortex (rat) . . . . .	19
Embryo (rat) . . . . .	23
Placenta (rat) . . . . .	15
Papilloma of bladder (man) . . . . .	26
Carcinoma of bladder (man) . . . . .	36
Rat sarcoma (Flexner-Jobling) . . . . .	31
Rat sarcoma (Jensen) . . . . .	34
Fowl sarcoma (Rous) . . . . .	30
Retina . . . . .	88

\*  $Q_M^{N_2}$ —lactic acid (cu. mm) formed in  $N_2$  per mg. dry weight of tissue per hour. 22,400 cu. mm. lactic acid = 90 mg. lactic acid.

It will be observed that very high rates of glycolysis are secured by brain cortex, retina, embryo and tumours.

The glycolytic activity of tumours is obviously of great significance; it is 120 times greater than that of blood.

Normal adult tissues usually show high rates of oxygen consumption (respiration) and little glycolysis. Embryonic tissues show both high respiration and high anaerobic glycolysis. Neoplastic tissues have high rates of anaerobic glycolysis and small respiratory rate. Retina, and to a less extent brain cortex, are exceptional

in showing high rates of anaerobic glycolysis and relatively high rates of respiration.

It is a commonly accepted conclusion that glycolysis provides the cell with an alternative supply of energy to that provided by respiration. Presumably the tumour cell equipped with a highly active glycolytic system is not so dependent on a supply of oxygen for its normal existence as an adult tissue cell, and this also applies to newly developing tissues such as the embryo.

The question as to whether glycolysis in embryo and tumour is of the phosphorylating or non-phosphorylating type is still unsettled.

Needham and Lehmann (*Biochem. J.* 1937, **31**, 1210) come to the conclusion that in the chick embryo there are two separate routes of carbohydrate breakdown, (1) a non-phosphorylating glycolysis depending greatly on the integrity of the cell structure, (2) a phosphorylating glycolysis similar to that of muscle but of much lower activity. Dialysis of minced embryo leads to inactivation of glycolysis which is partially restored by the addition of glutathione. They conclude also that methylglyoxal is not an intermediate in embryo glycolysis.

**AEROBIC GLYCOLYSIS AND THE PASTEUR EFFECT.**—Pasteur recognised that, in the absence of oxygen, yeast cells will ferment carbohydrate, but that admission of oxygen retards the rate of fermentation. Glycolysis in intact tissue cells (not in extracts) is similarly inhibited by the presence of oxygen and the phenomenon has been termed the "Pasteur Effect" by Warburg. (For a discussion of the Pasteur Effect, see Dixon, *ibid.* 1935, **29**, 973; 1936, **30**, 1479.)

Results (by Warburg) showing the relative rates of glycolysis of tissues in nitrogen ( $Q_M^{N_2}$ ) and in oxygen ( $Q_M^{O_2}$ ) are shown in Table II. The respiratory rates ( $Q_{O_2}$ —cu. mm.  $O_2$  absorbed per mg. dry weight of tissue per minute) are also given.

TABLE II.

Tissue	$Q_M^{O_2}$	$Q_M^{N_2}$	$Q_{O_2}$
Liver (rat) . . . . .	0.6	3.3	11.6
Kidney (rat) . . . . .	0	3.2	21.0
Testis (rat) . . . . .	7.2	8.5	12.3
Brain cortex (rat) . . . . .	2.5	19.1	10.7
Retina (rat) . . . . .	45.0	88.0	30.7
Embryo (chicken) . . . . .	1.1	20.6	10.0
Carcinoma (Flexner) . . . . .	25.0	31.0	7.2
Sarcoma (man) . . . . .	15.6	29.9	4.9

A noteworthy feature is the high aerobic glycolysis of tumour cells indicating the possibility that such cells may gain their energy for growth mainly from glycolysis even under aerobic conditions.

According to Crabtree (*ibid.* 1928, **22**, 1289) a high aerobic glycolysis may take place under pathological conditions in tissues. Warburg agrees (*Biochem. Z.* 1929, **204**, 482) that it is not specific for tumours.

There is no doubt, however, that, as a general



rule, respiration in a cell greatly represses its glycolysis. The mechanism by which this phenomenon takes place is not yet clear.

The view has been advanced that oxygen replaces pyruvic acid as a hydrogen acceptor in the Embden-Meyerhof sequence of reactions leading to glycolysis. Thus lactic acid formation would be inhibited or eliminated, water being formed instead. Szent-Gyorgyi ("Perspectives in Biochemistry," Cambridge, 1937, p. 172) hazards the view that in aerobic glycolysis, oxalacetic acid replaces pyruvic acid as a hydrogen acceptor in the Embden-Meyerhof scheme. Reduction of oxalacetic acid leads eventually to succinic acid which is oxidised by oxygen in the respiratory system of the cell back to oxalacetic acid. This hypothesis has as yet no experimental support.

The addition of a variety of substances to intact tissues may greatly increase the rate of aerobic glycolysis, up to that of anaerobic glycolysis, without appreciably affecting the respiratory rate. This phenomenon, known as the inhibition of the Pasteur effect, was first described in relation to fermentation. Warburg (Biochem. Z. 1926, **172**, 432) showed that carbylamine intensifies aerobic fermentation without any marked action on the respiration. Quastel and Wheatley (Biochem. J. 1932, **26**, 2169) showed that glutathione has a precisely similar action. Weil-Malherbe (*ibid.* 1938, **32**, 2257) finds that glutathione as well as glutamate increases aerobic glycolysis of brain. It is claimed that certain dyestuffs inhibit the Pasteur reaction (Elliott and Baker, *ibid.* 1935, **29**, 2396; Dickens, *ibid.* 1936, **30**, 661, 1064, 1233), and phenosafranine in particular has a powerful effect. Dickens (*ibid.* 1939, **33**, 2017) has recently shown that guanidine (M/1000) completely and reversibly inhibits the Pasteur effect in brain cortex slices. Certain substituted guanidines and amidines are even more powerful in their inhibitory influence on the Pasteur reaction, viz. 1:11-undecanediamidine and decamethylenediguanidine ("Synthalin") which are fully active at M/1,000,000. Excess of potassium ions (Ashford and Dixon, *ibid.* 1935, **29**, 157), lack of both potassium and calcium ions (Dickens and Greville, *ibid.* 1935, **29**, 1468) or the presence of ammonium ions (Weil-Malherbe, *ibid.* 1938, **32**, 2257) all effect the Pasteur reaction—conceivably through permeability changes in the cell membrane (Dixon and Holmes, *Nature*, 1935, **135**, 995).

Increase of temperature from 37° to 45° brings about a breakdown of the Pasteur effect and aerobic glycolysis increases to a high rate in spite of an increased respiratory rate (Dixon, Biochem. J. 1936, **30**, 1483).

#### Activators and Inhibitors of Glycolysis.

**Pyruvic Acid.**—Mendel, Bauch and Strelitz (Klin. Woch. 1931, **10**, 118) found that traces of pyruvic acid greatly increase anaerobic glycolysis, in tissues where glucose, and not glycogen, breakdown is responsible for lactic acid formation. Pyruvic acid appears to maintain glycolysis (of glucose) at a maximum level.

**POTASSIUM AND CALCIUM IONS.**—Ashford and Dixon (Biochem. J. 1935, **29**, 157) found that the

presence of M/10 KCl greatly increases aerobic glycolysis of brain but decreases anaerobic glycolysis. Dickens and Greville (*ibid.* 1935, **29**, 1468) reached a similar conclusion and showed the antagonistic effects of potassium and calcium ions on respiration. Quastel and Wheatley (J. Biol. Chem. 1937, **119**, 80P) found that calcium ions at low concentrations markedly increase anaerobic glycolysis and that strontium and magnesium have similar but smaller effects.

**DEPRIVATION OF OXYGEN AND OF GLUCOSE.**—Deprivation of brain tissue of both oxygen and of glucose for short periods (*e.g.* 5 minutes) very greatly decreases the rate of anaerobic glycolysis when glucose is subsequently added to the tissue (Dickens and Greville, Biochem. J. 1933, **27**, 1138). It had been concluded that anaerobiosis in the absence of glucose brings about irreparable damage to the brain. It was shown later, however (Quastel and Wheatley, *l.c.*), that if brain tissue which has been kept anaerobically in the absence of glucose is subsequently exposed to oxygen its power of bringing about anaerobic glycolysis is regained.

This fact, coupled with the facts that pyrophosphate breaks down rapidly in brain in absence of glucose and that aerobic resynthesis of adenylypyrophosphate takes place in brain (Engel and Girard, J. Biol. Chem. 1936, **112**, 379) lend support to the view that anaerobic glycolysis in brain takes place through the intermediate formation of phosphoric esters.

**IODOACETIC ACID.**—Iodoacetic acid at low concentrations suppresses glycolysis whether glucose or glycogen be the carbohydrate which is broken down. In muscle extracts iodoacetic acid inhibits the interaction of triosephosphate and pyruvic acid. Triosephosphate dehydrogenase is highly sensitive to iodoacetic acid (Rapkine, Biochem. J. 1938, **32**, 1729). Possibly the sensitivity of this enzyme to iodoacetic acid explains the latter's powerful inhibiting effects on glycolysis in muscle extracts.

Iodoacetic acid reacts rapidly with glutathione, a thioether being formed (Quastel and Wheatley, *ibid.* 1932, **26**, 2169; Dickens, *ibid.* 1933, **27**, 1141), and the problem has arisen as to whether this reaction accounts partly, or wholly, for the cessation of glycolysis in presence of iodoacetic acid. The reaction would obviously explain the highly inhibitory effect of iodoacetic acid on glyoxalase activity (Dudley). With our present limited knowledge of the influence of thiol compounds in glycolysis it is difficult to assess the importance of the reaction between iodoacetic acid and glutathione on the inhibition of glycolysis.

**SODIUM FLUORIDE.**—This substance at low concentration (M/200) suppresses glycolysis whether from glucose or from glycogen. Its inhibitory effect is presumably linked with the fact that it prevents the breakdown of phosphoglyceric acid into phosphopyruvic acid (Lohmann and Meyerhof, Biochem. Z. 1934, **273**, 60). Dickens and Simer (Biochem. J. 1929, **23**, 936) have shown that fluoride sensitivity of glycolysis varies in different organs.

**PHLORIPZIN.**—This substance inhibits yeast fermentation (Dann and Quastel, *ibid.* 1928, **22**, 245) and glycolysis in muscle extracts. Lunds-

gaard (Biochem. Z. 1931, **233**, 322) showed that phloridzin (M/100) inhibits phosphorylation of glycogen. According to Kalekar (Nature, 1935, **186**, 872) phloridzin prevents the formation of phosphoglyceric acid from triosephosphate.

**GLYCERALDEHYDE.**—Mendel (Klin. Woch. 1929, **8**, 169) found that *dl*-glyceraldehyde inhibits anaerobic glycolysis of glucose by tumours and that this inhibition can be reversed by the addition of pyruvic acid. Ashford confirmed this phenomenon for brain glycolysis, but Holmes (Ann. Rev. Biochem. 1934, **3**, 395) could find no inhibition of glycolysis of glycogen by glyceraldehyde in muscle extracts. Needham and colleagues (Biochem. J. 1937, **31**, 1165, 1210) find an inhibition of embryonic glycolysis by glyceraldehyde and conclude that this aldehyde specifically inhibits non-phosphorylating glycolysis (*see*, however, Adler and colleagues, Naturwiss. 1937, **25**, 282; Z. physiol. Chem. 1937, **249**, 40).

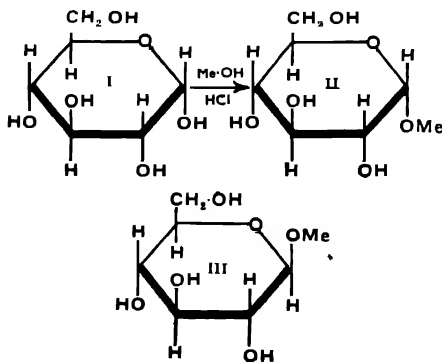
**OTHER INHIBITORS.**—The following substances also inhibit glycolysis (of glucose): hydroxymalonate (Jowett and Quastel, Biochem. J. 1937, **31**, 275); glutamate and  $\beta$ -hydroxyglutamate (Weil Malherbe, *ibid.* 1938, **32**, 2257); maleic acid (Morgan and Friedmann, *ibid.* 1938, **32**, 862).

**GLYCOLYSIS OF VARIOUS SUGARS.**—Mannose usually undergoes glycolysis under conditions where glucose is broken down to lactic acid. Fructose is broken down less rapidly than glucose by tumour slices and is also broken down by liver. It is, however, in common with galactose, but feebly attacked, with lactic acid liberation, by tumours, brain or chick embryo.

J. H. Q.

**"GLYCOSAL."** Trade name for a preparation of glycerol and salicylic acid.

**GLYCOSIDES.** Glycosides are formed by the condensation of one or more carbohydrate molecules with a non-carbohydrate, with elimination of one or more molecules of water. The junction involves a hydroxyl group of the non-carbohydrate, and the reducing or glycosidic hydroxyl of the sugar. Thus the simplest glycoside is formed from glucose and methyl alcohol by the catalytic action of hydrogen chloride:



The term "glycoside" refers to all compounds of this type, irrespective of the nature of the sugar (hexose, pentose, etc.) which is present.

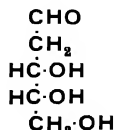
Strictly, the name "glucoside" is reserved for glycosides in which the sugar is glucose; the term is still, however, frequently applied to other glycosides. Galactosides, mannosides, etc., are glycosides in which the sugar is known to be galactose, mannose, etc.

Methylglycosides have not yet been found in nature, but glycosides of a more complex type are very abundant, occurring especially in the fruit, bark and roots of plants. Glycosides are in general readily hydrolysed by dilute acid, giving the free sugar or sugars and the non-carbohydrate portion of the molecule, which is conveniently referred to as the "aglycone." Hydrolysis of glycosides may also be effected by enzymes, which are usually present in the same plant tissue as the glycoside. If the cell tissue is destroyed, the enzyme comes into contact with the glycoside, and under suitable conditions (*e.g.* pH) hydrolysis will occur.

Corresponding with the two isomeric forms of glucose ( $\alpha$ -glucose, I), there are two series of glycosides, of which  $\alpha$ - and  $\beta$ -methylglucosides (II and III) may be regarded as the prototype. The enzyme emulsin hydrolyses many glycosides containing the  $\beta$ -linkage, but few, if any, with  $\alpha$ -linkages; conversely, the enzyme maltase hydrolyses the  $\alpha$ -bond in maltose, but not the  $\beta$ -linkage in the corresponding disaccharide cellobiose. Such reactions frequently afford evidence of the nature of the bond in glycosides. Other possibilities of isomerism exist in the sugar series, especially in the nature of the heterocyclic ring, which may, for instance, be pyranose (6-atom) or furanose (5-atom) (*v.* CARBOHYDRATES). Investigation of the sugar portion of a glycoside requires evidence upon all such points.

#### THE CARBOHYDRATES OF NATURAL GLYCOSIDES.

Whilst glucose is by far the most common sugar found in natural glycosides, galactose also frequently occurs. The pentoses arabinose and xylose, and the methylpentose rhamnose (*v.* Vol. II, 287c), occur widely, whilst the sugars of the cardiac glycosides have been shown recently to be of the 2:6-deoxyhexose type, digitoxose (*v.* Vol. II, 381c), and cymarose (*v.* Vol. III, 538b), which have not yet been found elsewhere in nature. The branched chain pentose, apiose (*v.* Vol. I, 450c) is one of the constituents of apinin. It is interesting to note that 2-deoxy-*d*-ribose,



occurs in nucleic acid.

Uronic acids, although common in polysaccharides, rarely occur in glycosides. Euxanthic acid, a glucuronic acid, is a product of animal metabolism and is not otherwise found in nature. Baicalein is a flavone glycoside containing glucuronic acid.

Where 2 mol. of carbohydrate are found in

a glycoside, they may be present as a disaccharide (biose). Common disaccharides of this type are given in the table below, together with some glycosides in which they occur.

Disaccharide.	Structure.	Occurrence.
Gentiobiose	6-( $\beta$ - <i>D</i> -glucosido)- <i>D</i> -glucose	Amygdalin, crocin.
Vicianose	6-( $\beta$ - <i>L</i> -arabosido)- <i>D</i> -glucose	Vicianin, violutolose, gein.
Primeverose	6-( $\beta$ - <i>D</i> -xylosido)- <i>D</i> -glucose	Monotropitin, primeverin, primulaverin.
Rutinose	6-( $\beta$ - <i>L</i> -rhamnosido)- <i>D</i> -glucose	Rutin, datiscin.

It is interesting to note the prevalence of 1-6- $\beta$ -linkages in these bioses. Some trisaccharides are found in glycosides, but their constitution is, in most cases, not established. Robinose, obtained from the glycoside robinin, appears to be of the rhamnose-galactose-rhamnose type.

The ring structures of the sugars in the natural glycosides are chiefly pyranose, but the ribose and 2-deoxyribose in nucleosides have a furanose configuration (Levene and Tipton, *J. Biol. Chem.*, 1932, **94**, 809). Furanose pentoses are now being found frequently in nature in the plant gums. The majority of polysaccharides have linkages of the glycosidic type and therefore are glycosides from that point of view.

In general, one form (*D*- or *L*-) of the possible optical isomers of a sugar predominates in nature. Thus *D*-glucose, *D*-mannose and *L*-rhamnose are the only naturally occurring forms of these sugars which have been, so far, identified, but *L*-arabinose is the chief constituent of the plant gums whilst *D*-arabinose occurs in the glycosides barbaloin and isobarbaloin.

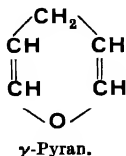
Most natural glycosides are of the  $\beta$ -type, they are hydrolysed by the enzyme emulsin and are therefore laevo-rotatory (*cf.*  $\beta$ -methylglucoside).

#### THE MAIN TYPES OF GLYCOSIDES FOUND IN NATURE.

The types of glycosides found in nature vary widely, but may be roughly grouped as follows, according to their non-carbohydrate constituents (aglycones):

(a) **Phenolic Glycosides.**—The aglycones include *o*-hydroxybenzyl alcohol (in salicin), quinol (in arbutin), coniferyl alcohol (in coniferin). The sugar molecule is attached to the phenolic hydroxyl group. Nearly related are the hydroxyanthraquinone nucleus, which occurs in ruberythric acid, rubiadin and purpurin, etc., and the hydroxycoumarin nucleus, present in aesculin, daphnin, etc.

(b)  **$\gamma$ -Pyran Derivatives.**—This group includes many of the most important glycosides. The majority of red and blue plant- and berry-pigments, anthocyanins (*q.v.*) are derivatives of  $\gamma$ -pyran.



Closely related are the flavone, flavonol and xanthone pigments, which constitute a large proportion of the yellow dyes of flowers, roots and woods. Chrysin, quercitrin and euxanthone

respectively are typical examples of these three classes, which may occur without any combined sugars. Quercitrin-3-rhamnoside is the glycoside quercitrin.

(c) **Steroid Glycosides.**—The aglycones of the important digitalis glycosides and of some of the saponins are related to the sterols. The powerful physiological properties of these glycosides, and their structural similarity to the hormones, the bile acids and vitamin D, are of great interest (*v. CARDIAC GLYCOSIDES*).

Saponins have similar physiological properties to the cardiac glycosides. They produce a stable foam on agitating an aqueous solution even at great dilution, have a bitter taste, irritate the mucous membrane and hamolyse red blood corpuscles in very low concentration (1:168,000 for digitonin). Administered intravenously they are therefore very poisonous.

(d) **Purine and Pyrimidine Glycosides.**—The nucleic acids, which in combination with protein material appear to constitute the main portion of the nuclei of plant and animal cells, yield on hydrolysis nucleosides, which are glycosides formed by the combination of purine or pyrimidine bases with a sugar. The latter is frequently *D*-ribose or 2-deoxy-*D*-ribose, with a furanose ring structure. Typical aglycones are adenine, guanine and cytosine.

(e) **Nitriles** frequently occur combined with sugars, forming the cyanogenetic or cyanophoric glycosides (*q.v.*). The well-known glycoside amygdalin (*q.v.*) is of this type.

(f) **Sulphur Compounds.**—A number of plants yield glycosides which contain sulphur and which on hydrolysis give mustard oils of the allyl isothiocyanate type, and a sugar. Sinigrin (p. 96a) and sinalbin (p. 95d) are typical examples of such glycosides, occurring in the seeds of the black and white mustard respectively. These glycosides are in general hydrolysed by a specific enzyme occurring in the same plant, *e.g.* myrosinase.

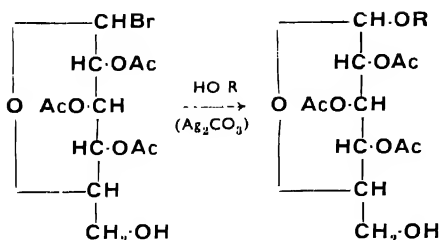
Certain important glycosides (*e.g.* riboflavin, vitamin B<sub>2</sub>) and indican (3- $\beta$ -glucosido-oxyindole) are not readily classified, whilst others have so far been insufficiently investigated.

#### SYNTHESIS OF GLYCOSIDES.

(a) The simple glycosides are most readily prepared by the direct interaction of the alcohol ( $\text{CH}_3\cdot\text{OH}$ ,  $\text{C}_2\text{H}_5\cdot\text{OH}$ , etc.) with the sugar, in the presence of hydrogen chloride (c. 1%) as a catalyst (Fischer, *Ber.* 1893, **26**, 2400). In this way a mixture of the  $\alpha$ - and  $\beta$ -forms of the glycoside is obtained, which may usually be separated partially by fractional crystallisation.

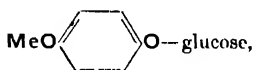
(b) A more selective method uses a sugar derivative of the acetobromoglucose type, which condenses with a hydroxyl group of the

aglycone, the HBr being removed by silver carbonate.



The acetyl groups are usually removed by alcoholic ammonia at 0°, giving the desired glycoside. It should be noted that a Walden inversion occurs in this reaction, and if  $\alpha$ -acetobromoglucose is used, then the  $\beta$ -glucoside is obtained, and *vice versa*. The normal method of preparation of acetobromo-sugars (by the action of hydrogen bromide in glacial acetic acid upon the penta-acetate of the sugar) yields the  $\alpha$ -isomeride as the chief product, even if the  $\beta$ -penta-acetate is used, and this procedure therefore results in the formation of  $\beta$ -glycosides only. If, however, quinoline is used in place of silver carbonate in the condensation, a mixture of  $\alpha$ - and  $\beta$ -glycosides is formed (Fischer and Von Mechel, Ber. 1916, 49, 2813). Further,  $\beta$ -methylglucose tetra-acetate may be transformed nearly quantitatively into  $\alpha$ -methylglucoside tetra-acetate by heating with titanium tetrachloride in chloroform solution (Pacsu, *ibid.* 1928, 61 [B], 137, 1513).

The corresponding chloro-compound, aceto-chloroglucose, may also be used in this reaction. In this way Michael (*ibid.* 1881, 14, 2097) obtained methylarbutin,



the first naturally occurring glycoside to be synthesised. Acetobromoglucose has been used extensively by Robinson in his extensive syntheses of anthocyanins (*e.g.* of malvin, J.C.S. 1932, 2299).

The synthesis of glycosides by means of enzymes falls into a somewhat different category, but may be mentioned here. Bourquelot (series of papers, Compt. rend. 1912-15) found that enzymic hydrolysis of glycosides is reversible, and sugars may be made to combine with alcohols by the use of enzymes (*e.g.* emulsin) under appropriate conditions. Thus Hérissay (*ibid.* 1921, 172, 1536; 173, 1406) obtained  $\alpha$ -methylmannoside by the action of an enzyme, seminase (present in germinated lucerne seeds), upon a solution of mannose in 10% methyl alcohol. Other methods for the synthesis of glycosides are given in Tollens-Elsner, "Kurztes Handbuch der Kohlenhydrate," 4th ed., Leipzig, 1935, p. 45.

#### GENERAL PROPERTIES OF GLYCOSIDES.

The simple glycosides (*e.g.* methylglucosides) are colourless, crystalline solids, readily soluble

in water and alcohol, and nearly insoluble in ether. They are optically active, hydrolysed by acids with varying ease, but comparatively stable to the action even of concentrated alkali. They are non-reducing to Fehling's solution and to alkaline iodine (as regards their sugar portions).

The size and active groups of the aglycone obviously influence the properties of the glycoside, although the hydroxyl groups in the carbohydrate continue to make the compound soluble in water, even if the aglycone is of the sterol type (*e.g.* the saponins). In general, the properties of the glycoside may be regarded as the sum of the properties of the two components. Some glycosides (*e.g.* saponins) are amorphous and difficult to obtain in a state of purity.

The relationship between the rate of hydrolysis of glycosides, the critical increment and their constitution has been investigated by Moelwyn-Hughes (Trans. Faraday Soc. 1928, 24, 309; 1929, 25, 81, 503).

#### HYDROLYSIS OF GLYCOSIDES BY ENZYMES.

Owing to the extreme difficulty of characterising preparations of enzymes it is not surprising that a mass of conflicting evidence has been accumulated upon this subject, but certain well-established facts may be mentioned. The chief enzyme preparations in this field are emulsin, maltase and invertase. Emulsin, extracted from bitter almonds, is a mixture of enzymes, of which the outstanding function is the hydrolysis of  $\beta$ -glucosides, *e.g.* amygdalin, gentiobiose,  $\beta$ -methyl-*d*-glucoside. The presence of an  $\alpha$ -glucosidase and  $\alpha$ -mannosidase in emulsin has been reported (Helferich and co-workers, Z. physiol. Chem. 1932, 214, 139; 215, 277; 216, 123). Maltase is present in yeast and effects the hydrolysis of  $\alpha$ -glucosides in general, *e.g.* maltose,  $\alpha$ -methylglucoside. Invertase is also present in yeast and hydrolyses  $\beta$ -fructosides such as sucrose. The action of emulsin and maltase appears to be of a general nature, *i.e.* nearly all  $\beta$ - or  $\alpha$ -glucosides, respectively, are attacked. Myrosinase similarly hydrolyses the " $\text{S}$ —glucose" linkage in the mustard-oil glycosides. Other enzymes appear to be more specific in nature and hydrolyse special carbohydrate configurations only, *e.g.* indimulsin hydrolyses indican, vicinase hydrolyses vicianin (*d*-mandelonitrile-vicianoside) and neither seems to attack any general group of glycosides. Weidenhagen has proposed a theory concerning the specificity of carbohydrases, in which the action of an enzyme is determined by the ring structure, configuration and  $\text{C}_1$  stereoisomerism of the substrate, but not by the non-sugar portion (Weidenhagen, *ibid.* 1933, 216, 255; Angew. Chem. 1934, 47, 451). There is substantial experimental evidence against this view (*see, for example, Hestrin, Biochem. J.* 1940, 34, 213, where further references are given).

The effect of various changes in the constitution of glycosides upon the rate of hydrolysis by enzymes has been investigated by Helferich (Z. physiol. Chem. 1937, 248, 85; Annalen, 1937, 531, 160; 534, 276).

### THE BIOLOGICAL SIGNIFICANCE OF GLYCOSIDES.

Various proposals have been made as to the function of glycosides in plants. They may be waste materials, being the form in which toxic compounds such as phenols and sterols are made soluble and removed. Bunge has made the interesting suggestion that their rôle is bactericidal; when the tissue is damaged the enzyme hydrolyses the glycoside, liberating the aglycone, which is frequently antiseptic (e.g. phenols), and prevents the harmful action of micro-organisms. The subject is discussed by E. F. and K. F. Armstrong, "The Glycosides," Longmans, 1931.

The occurrence of a glycoside in several different plant types is of interest, and in the list of natural glycosides which follows, mention is made of such distributions. In some cases, glycosides of very different types are found in the same source; thus horse-chestnuts (from *Æsculus hippocastanum*) contain æscin (a steroid of the saponin type) and æsculin (a coumarin glycoside). The presence of crocin (a carotenoid) in some species of crocus and of picrocrocin (a terpene glycoside) in other species is noteworthy because carotenoids and terpenes are generally regarded as being formed from isoprene units.

**Bibliography.**—An excellent account of the cardiac glycosides is given in Fischer's "The Chemistry of Natural Products Related to Phenanthrene," 2nd ed., Reinhold Publ. Corp., New York, 1937. Developments in the field of anthocyanins have been reviewed by Robinson in a series of papers, including Nature, 1935, 135, 732; 1936, 137, 94; 1938, 142, 356. A general review of the subject is given by E. F. and K. F. Armstrong (*op. cit.*).

An alphabetical list of glycosides found in nature now follows, in which the literature has been reviewed up to and including 1938. The structures of glycosides belonging to the important group of the anthocyanins are given with reference to a "type formula" to be found in the survey of the various types of glycosides, earlier in this introduction. Glycosidic links (from the reducing hydroxyl group of the sugar) are to be assumed unless it is otherwise stated, and if a glycoside is hydrolysed by emulsin it is normally a  $\beta$ -glycoside. The specific rotation quoted is measured in aqueous solution unless the solvent is stated. The activity of some cardiac glycosides has been given, expressed in frog-doses per mg. (F D./mg.).

**Acacian** (v. Vol. I, 12).

**Acacipetalin**,  $C_{11}H_{17}O_6N$ , m.p. 176-7°,  $[\alpha]_D -36.6^\circ$ , is a cyanogenetic glucoside from *Acacia* species. Complete hydrolysis (alkali and then acid) yields *d*-glucose and isobutyrylformic acid (Rimington, 1937, A., 11, 136). It appears to be dimethyketen cyanohydrin  $\beta$ -glucoside.

**Acertannin**,  $C_{26}H_{26}O_{13}$ , m.p. 165°,  $[\alpha]_D +21^\circ$  (acetone), occurs in *Acer ginnale*. It is probably the digalloyl derivative of an anhydrohexitol (Fischer and Freudenberg, Annalen, 1911, 384, 238; Perkin and Uyeda, J.C.S. 1922, 121, 66).

**9-Adenine-thiomethylpentoside** has been found in yeast extracts (Mandel and Dunham, J. Biol. Chem. 1912, 11, 85; Suzuki *et al.*, Biochem. Z. 1924, 154, 278; Levene, J. Biol. Chem. 1924, 59, 465; *ibid.* 1925, 65, 551; Sobotka, *ibid.* 1926, 69, 267). Falconer and Gulland (J.C.S. 1937, 1912) have shown that the sugar is attached to position 9 in the adenine molecule. The constitution of the sugar is not yet known.

**Adenosine**,  $C_{10}H_{13}O_4N_5 \cdot \frac{1}{2}H_2O$ ,  $[a]_D -60^\circ$ , 9-adenine-*d*-ribofuranoside, has been isolated from heart-muscle and from yeast, and is a component of their nucleic acids. Acid or enzymic hydrolysis gives *d*-ribose and adenine (Levene and Jacobs, Ber. 1909, 42, 2703). Monophosphoric esters of adenosine occur as muscle-adenylic acid and yeast-adenylic acid; the latter has the phosphoric acid residue in position 3 of the ribose. Adenosinetriphosphate occurs in muscle extract (Lohmann, Naturwiss. 1928, 16, 298; 1929, 17, 624) and plays an important part in sugar metabolism in animals and plants and in alcoholic fermentation (the position of the ribose side-chain is discussed by Gulland and Holiday, J.C.S. 1936, 765) (v. Vol. V, 186).

**Adonidoside**, **Adonivernoside**, are cardiac glycosides isolated from *Adonis vernalis* (Mercier and Mercier, Rev. Pharmacol. 1927, 1, 1). Their physiological activities are 600 and 300 F.D./mg. respectively (v. Vol. II, 387b).

**Æscin**,  $C_{55}H_{88}O_{27}$ , (decomp. 220-230°), is a saponin occurring in horse-chestnut seeds (*Æsculus hippocastanum*). Hydrolysis is reported to give glucose, glucuronic acid and æscigenin (v. Vol. I, 160c), which appears to be a triterpenoid of the hederagenin type (see Hederin, p. 89d), since on dehydrogenation it yields sapotalin. Its constitution is not yet known (Chem. Zentr. 1929, II, 2780). (See also Winterstein, Z. physiol. Chem. 1931, 199, 25; Burcs and Babor, Chem. Zentr. 1935, I, 3936; 1937, II, 403.)

**Æsculin** (v. Vol. I, 160).

**Aloin** (v. Vol. I, 262a)

**Althæin**,  $C_{22}H_{23}O_{12}Cl$  (chloride), is an anthocyanin occurring in black mallow (*Althaea rosea*). Hydrolysis yields glucose (1 mol.) and myrtillidin chloride, which is the 7-methyl ether of delphinidin chloride (v. Vol. III, 554d) (Willstätter and Martin, Annalen, 1915, 408, 110; Chem. Zentr. 1930, I, 3193). (Cf. Karrer and Weber, Helv. Chim. Acta, 1936, 19, 1025, who find althæin to be a mixture of various anthocyanins) (v. Vol. I, 264a).

**Amolonin** is a crystalline saponin present in the Californian soap plant, *Chlorogalum pomeridianum* (Jurs and Noller, J. Amer. Chem. Soc. 1936, 58, 1251). Amolonin has the probable molecular formula  $C_{63}H_{104}O_{31}$ . Hydrolysis gives *d*-glucose (3 mol.), *d*-galactose (1 mol.), *l*-rhamnose (2 mol.) and a sterol, tigogenin, identical with the aglycone of tigonin (p. 97a).

**Ampelopsin** (*q.v.*).

**Amygdalin** (*q.v.*).

*iso*-Amygdalin is *dl*-mandelonitrile  $\beta$ -gentiobioside.

**Androsin** (*q.v.*). For synthesis, see Mauthner,

J. pr. Chem. 1918, [ii], 97, 217; 1925, [ii], 110, 123).

**$\alpha$ -Antiarin,  $\beta$ -Antiarin** (v. Vol. II, 387c).  $\alpha$ -Antiarin on hydrolysis gives a sugar, antiarose, of unknown structure (isomeric with rhamnose);  $\beta$ -antiarin gives rhamnose (Tschesche, Ber. 1936, 69 [B], 1377).

**Apiin** (q.v.).

**Aralin** is a saponin of the hederin type (p. 89c) found in varieties of *Aralia* (Winterstein and Stein, Z. physiol. Chem. 1932, 211, 5).

**Arbutin** (v. Vol. I, 457c). (Purification of arbutin to m.p. 199.5–200°,  $[\alpha]_D -64.3^\circ$ , has been reported by Reichert and Turkowitsch, Arch. Pharm. 1938, 276, 397.) The rate of hydrolysis and its activation energy have been measured by Moelwyn-Hughes (Trans. Faraday Soc. 1929, 25, 503).

The blackening of the leaves of certain varieties of *Pyrus* is due to hydrolysis of arbutin by enzymes present; the liberated hydroquinone is readily oxidised to give a black product. Leaves containing much methylarbutin turn yellow and then black, owing to the different oxidation reactions of methylhydroquinone.

**Asperulin** (q.v.).

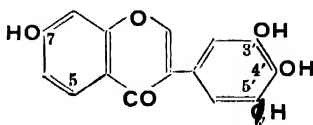
**Attractylic Acid**,  $C_{30}H_{48}O_{18}S_2K_2$  (potassium salt), m.p. 173°,  $[\alpha]_D -64^\circ$ , appears to be of the mustard-oil glucoside type. It is the poisonous principle of the roots of *Atractylis gummifera* (*Carlina gummifera*) (Chem. Zentr. 1920, II, 614) and is of unknown constitution. Acid hydrolysis gives glucose, valeric acid (2 mol.), potassium hydrogen sulphate (2 mol.) and an unidentified aglucone,  $C_{14}H_{22}O_4$  (Wunschendorff and Braudel, *ibid.* 1932, II, 70; see also Ajello, *ibid.* 1933, II, 2399; Wunschendorff and Valier, *ibid.* 1934, I, 3752, 3861).

**Aucubin** (q.v.).

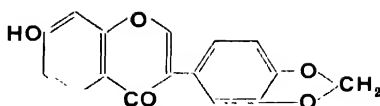
**Avenin** (glucovanillin),  $C_{14}H_{18}O_8$ , m.p. 192°,  $[\alpha]_D -88.6^\circ$ , is found in *Avena sativa* and *Triticum repens*. It appears to be a glucoside of vanillin (see Fischer and Raske, Ber. 1909, 42, 1465). It is an oxidation product of the glucoside coniferin (q.v.). Vanillin  $\beta$ -glucoside has been synthesised (Thorpe and Williams, J.C.S., 1937, 494).

**Baicalin** (q.v.). An enzyme, prepared from *Prunus armeniaca* var. *ansu* consists of baicalinase and  $\beta$ -glucosidase (Miwa, Amer. Chem. Abstr. 1936, 8272; Shibata and Hattori, Acta. Phytolum. 1930, 5, 117; Miwa, *ibid.* 1932, 6, 155; 1935, 8, 231; 1936, 9, 89).

**Baptisin**,  $C_{27}H_{31}O_{15}$ , m.p. 240°,  $[\alpha]_D -61^\circ$ , occurs with  $\psi$ -baptisin in the roots of *Baptisia tinctoria*. Hydrolysis with acid gives *l*-rhamnose (2 mol.) and baptigenin.  $\psi$ -Baptisin on hydrolysis gives *d*-glucose, *l*-rhamnose and  $\psi$ -baptigenin (Spath and Schmidt, Monatsh. 1929, 53/54, 454).



Baptigenin.



$\psi$ -Baptigenin.

The position of the sugar residues in baptisin is not settled.

**Barbaloin** (v. Vol. I, 262a).

**Butrin**,  $C_{27}H_{32}O_{15} \cdot 2H_2O$ ,  $[\alpha]_D -81.7^\circ$  (in pyridine), has been isolated from *Butea frondosa* flower (Lal, J.C.S. 1937, 1562; J. Indian Chem. Soc. 1935, 12, 262). Hydrolysis gives glucose (2 mol.) and 7:3':4'-trihydroxyflavanone. The sugars are present as a bioside.

**Callistephin** (q.v.).

**Camellia-Saponin**,  $C_{57}H_{94}O_{30} \cdot 6H_2O$ , m.p. 208° (anhydrous),  $[\alpha]_D +37^\circ$ , is a saponin of the hederin type (v. p. 89) found in *Camellia japonica*. Hydrolysis gives glucose (3 mol.), arabinose (2 mol.) and camellia-sapogenin,  $C_{29}H_{44}O_5$ , decomp. 194–197° (Aoyama, Chem. Zentr. 1929, I, 248), of unknown structure. On dehydrogenation the sapogenin yields sapotalin (1:2:7-trimethylnaphthalene), suggesting that it is similar in structure to hederagenin (p. 89d).

**Cerberin** (v. Vol. II, 481). A cardiac glycoside (Vol. II, 387c).

**Cetyl d-Glucoside**,  $C_{22}H_{41}O_8$ , m.p. 150°,  $[\alpha]_D -22^\circ$ , occurs in the *Sarsaparilla* root. It has been synthesised from cetyl alcohol and acetobromoglucose (Fischer and Helferich, Annalen, 1911, 383, 79; Salway, J.C.S. 1913, 103, 1022).

**Chebulinic Acid**,  $C_{41}H_{34}O_{27}$ ,  $[\alpha]_D +15^\circ$  (MeOH– $H_2O$ ), occurs in the fruit of *Terminalia hebula*. Hydrolysis by dilute alkali or by tannase gives *d*-glucose, gallic acid (3 mol.) and a dibasic acid of unknown structure (Freundenberg, Ber. 1919, 52 [B], 1238; 1920, 53, [B], 1728). One carboxyl group of this acid appears to be condensed with the glucosidic hydroxyl group and at least two of the gallic acid molecules are attached to the glucose (Freundenberg and Frank, Annalen, 1927, 452, 303).

**Cheiranthin** (q.v.).

**Chellol-Glucoside**,  $C_{19}H_{26}O_{10} \cdot 2H_2O$ , m.p. 175°, occurs in Arabian "chellah," *Amni visnaga*. Acid hydrolysis gives *d*-glucose and a substance of the coumarin type of unknown constitution (Fantl and Salem, Biochem. Z. 1930, 226, 166).

**Chrysanthemin** (q.v.).

**Cichoriin** (q.v.).

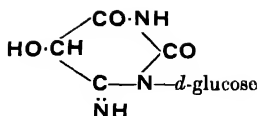
**Citronin**,  $C_{28}H_{34}O_{14}$ , m.p. 235°, occurs in various species of *Citrus* (cf. Naringin). Hydrolysis gives *d*-glucose, *l*-rhamnose and citronetin,  $C_{16}H_{14}O_6$ , m.p. 225°, which is 5:7-dihydroxy-2'-methoxyflavanone (Shinoda and Sato, Chem. Zentr. 1931, II, 2326; Yamamoto and Oshima, Amer. Chem. Abstr. 1932, 26, 1295).

**Clavicepsin** (q.v.).

**Coniferin** (q.v.).

**Convallatoxin** (v. Vol. II, 387b).

**Convicine**,  $C_{16}H_{15}N_3O_8 \cdot H_2O$ , is a pyrimidine glucoside occurring with vicine (v. p. 97d) in vetch seeds (Ritthausen). It appears to have the formula given at the top of the next page.



(See Johnson, J. Amer. Chem. Soc. 1914, **36**, 357; Fisher and Johnson, *ibid.* 1932, **54**, 2038.)

**Convolvulin** (*q.v.*). See also Mannich and Schumann, A., 1938, II, 238.

**Coronillin** (*q.v.*).

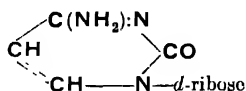
**Crocin** (*q.v.*).

**Cyanin** (*q.v.*).

**Cyclamin**,  $\text{C}_{56}\text{H}_{98}\text{O}_{20}$ , decomp.  $254^\circ$ , a saponin of the hederin type (p. 89) found in alpine violets (*Cyclamen europaeum*) (Plzák, Ber. 1903, **36**, 1761; cf. Chem. Zentr. 1927, I, 2331; 1929, I, 2655). Hydrolysis gives glucose (3 mol.), arabinose (2 mol.) and cyclamiretin,  $\text{C}_{28}\text{H}_{46}\text{O}_4$  (Dafert *et al.*, Chem. Zentr. 1926, II, 2437; 1930, I, 1798; 1934, II, 1785 (revision of molecular formulae)). The last compound gives saponatin on dehydrogenation. Its structure is not yet known.

**Cymar** (*q.v.*).

**Cytidine** is a pyrimidine nucleoside (cf. Uridine, p. 97b) formed on hydrolysis of yeast-nucleic acid. It is 3-cytosine *d*-ribofuranoside.



In the nucleic acid, the hydroxyl group in position 3 of the ribose is esterified with phosphoric acid (Levene and London, J. Biol. Chem. 1929, **83**, 793).

**Daidzin**,  $\text{C}_{21}\text{H}_{20}\text{O}_9$ , m.p.  $235^\circ$ ,  $[\alpha]_D -37^\circ$ , is an isoflavone glucoside from *Soja hispida* (cf. Genistin, p. 88c). Hydrolysis gives *d*-glucose and daidzein (*v. Vol. V*, 259c).

**Daphnin** (*q.v.*).

**Datiscin** (*v. Vol. III*, 549c).

**Delphin** (*q.v.*).

**Delphinin** (*q.v.*).

**Deoxyadenosine, deoxycytidine, deoxyguanosine, deoxyuridine**.—These purine nucleosides are hydrolysis products of nucleic acids, and are similar in structure to adenosine, cytidine, guanosine and uridine respectively, having deoxy-*d*-ribofuranose in place of *d*-ribofuranose. They are obtained by enzymatic cleavage, as deoxyribose is very sensitive to chemical reagents (Levene and London, J. Biol. Chem. 1929, **81**, 711; 1929, **83**, 793). Gulland and Story (J.C.S. 1938, 259) have shown that in deoxyadenosine the sugar is attached to position 9.

**Dhurrin** (*q.v.*).

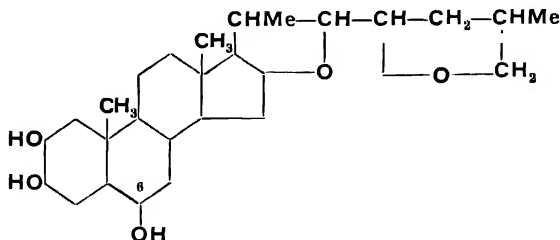
**Dibenzoylglucosylose**,  $\text{C}_{25}\text{H}_{24}\text{O}_{12}$ , m.p.  $148^\circ$ ,  $[\alpha]_D -107^\circ$ , occurs in the branches of *Daviesia latifolia* (Power and Salway, J.C.S. 1914, **105**, 767, 1062; Tutin, *ibid.*, 1915, **107**, 7). Alkaline hydrolysis gives benzoic acid and glucosylose, a disaccharide,  $[\alpha]_D -36.5^\circ$ , non-reducing to Fehling's solution and giving no osazone. It appears to be *d*-xylosido-*d*-glucoside, the two glycosidic hydroxyl groups forming the linkage between the sugars.

**Diglanides (A, B and C)** (*v. Vol. II*, 385).

**Diginin** (*v. Vol. II*, 384d).

**Digitalin** (*v. Vol. II*, 384d).

**Digitonin** is a saponin, occurring with several cardiac glycosides of somewhat similar constitution (*e.g.* digitoxin) in the leaves of *Digitalis purpurea*. It is one of the few well-characterised saponins. Its isolation in a pure state is nevertheless difficult. Cardiac glycosides are removed from the crude extract by chloroform or ether. Digitonin is then separated from other saponins (gitonin, tigonin, etc.) by fractional precipitation with amyl alcohol (Kihara, Ber. 1910, **43**, 3562; 1916, **49**, 701) or as an adduct with ether (Windaus, Z. physiol. Chem. 1925, **150**, 205). Repetition of these methods gives pure digitonin. It has the probable molecular formula  $\text{C}_{56}\text{H}_{92}\text{O}_{20}$ , m.p.  $235^\circ$ . Hydrolysis gives glucose (2 mol.), galactose (2 mol.), xylose (1 mol.) and the steroid *digitogenin*,  $\text{C}_{27}\text{H}_{44}\text{O}_6$ , m.p.  $253^\circ$ , which appears to have the following structure (see Tschesche and Hagedorn, Ber. 1936, **69** [B], 797):



**Digitoxin** (*v. Vol. II*, 384b).

**Digoxin** (*v. Vol. II*, 385b).

**Diosmin** (Barosmin),  $\text{C}_{34}\text{H}_{44}\text{O}_{21}$ , m.p.  $280^\circ$  (*v. Vol. IV*, 8c).

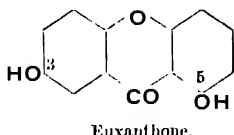
**Dryophantin**,  $\text{C}_{23}\text{H}_{28}\text{O}_{15}$ , m.p.  $220^\circ$ , occurs in galls produced by *Dryophanta*, on *Quercus* species. Hydrolysis gives glucose (2 mol.) and purpurogallin, m.p.  $275^\circ$  (Nierenstein, J.C.S. 1919, **115**, 1328).

**Emicymarin**,  $\text{C}_{30}\text{H}_{46}\text{O}_9$ , is a glycoside isolated from the seeds of *Strophanthus emini* by Lamb and Smith (*ibid.* 1936, 442) by partial enzymatic hydrolysis. Acid hydrolysis gives digitalose (*q.v.*) and a steroid trianhydroperiplogenin (see Periplocymarin, p. 93a).

**Erysolin** (see Glucocheirolin, p. 88d).

**Euxanthic Acid** (*q.v.*),  $\text{C}_{10}\text{H}_{16}\text{O}_{10} \cdot 3\text{H}_2\text{O}$ , m.p.  $162^\circ$  is the glycoside present in Indian

yellow (Kostanecki, Ber. 1886, **19**, 2918). Hydrolysis gives *d*-glucuronic acid and euxanthone, 3:5-dihydroxyxanthone, m.p. 237° (Graebe, Ber. 1899, **22**, 1405).



The uronic acid is attached to position 3 and has a pyranose structure (Robertson and Waters, J.C.S. 1931, 1709).

**Floridoside**,  $C_9H_{16}O_8$ , m.p. 87°,  $[\alpha]_D +151^\circ$ , occurs in *Rhodymenia palmata*. Hydrolysis by acid or yeast gives galactose (1 mol.) and glycerol. It is not hydrolysed by emulsin, and it is therefore probably an  $\alpha$ -galactoside (Colin and Augier, Chem. Zentr. 1933, **1**, 3953). It is probably  $\beta$ -( $\alpha$ -*d*-galactosido)-glycerol (Colin, Bull. Soc. chim. 1937, [v], **4**, 277).

**Folinarin** has been shown to be identical with oleandrin (p. 92c) (Neumann, Ber. 1937, **70** [B], 1547; Tschesche, *ibid.* 1554).

**Frangulin** (Franguloside) is a glycoside of the anthraquinone type, giving rhamnose and 4:5:7-trihydroxy-2-methylanthraquinone on hydrolysis. It occurs in *Rhamnus frangula* (Bridel and Charaux, Compt. rend. 1930, **191**, 1151).

**Fraxin**,  $C_{16}H_{18}O_{10}$ , m.p. 205°, is a coumarin glucoside found in the ash (*Fraxinus excelsior*) and species of *Besulus*. Hydrolysis by emulsin or acids gives *d*-glucose and fraxetin, 6-methoxy-7:8-dihydroxycoumarin, m.p. 227–228°. The glucose is attached to position 8 (Wessely and Denner, Ber. 1928, **61** [B], 1279, 1929, **62** [B], 120; Wessely and Lechner, Monatsh. 1932, **60**, 159).

**Fustin**,  $C_{26}H_{28}O_4$ , m.p. 330°, has been described as a flavonol glycoside occurring in the stems and branches of young fustic (*Rhus cotinus*) and in *Quebracho colorado*. Hydrolysis was said to give rhamnose (1 mol.) and fisetin (2 mol.),  $C_{15}H_{10}O_6$ , m.p. 219°. Fisetin is 3:7:3':4'-tetrahydroxyflavone (A. G. Perkin, J.C.S. 1897, **71**, 1194; Allan and Robinson, *ibid.* 1926, 2334).

Recently, however, it has been claimed that fustin is dihydrofisetin, and gives no sugars on hydrolysis (Oyamada, J. Chem. Soc. Japan, 1934, **55**, 755; **56**, 980).

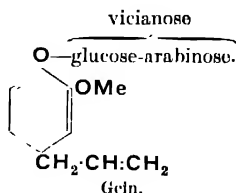
**Galuteolin**,  $C_{21}H_{20}O_{11}$ , m.p. 280°, is a flavone glycoside isolated from the seeds of *Galega officinalis*. Hydrolysis gives glucose and luteolin (v. Vol. IV, 189a), the dye of *Reseda luteola* which when dried is known as "dyer's weed" (Barger and White, Biochem. J. 1923, **17**, 836; Chem. Zentr. 1931, **II**, 2464).

**Gaultherioside**,  $C_{15}H_{24}O_{10}$ , m.p. 185°,  $[\alpha]_D -58^\circ$ , is present in fresh *Gaultheria procumbens*. It is non-reducing. Hydrolysis yields glucose, xylose and ethyl alcohol (Rabaté and Rabaté, Chem. Zentr. 1931, **II**, 1711). The sugars are present as the biiose primeverose (cf. Primeverin, p. 94a); it is therefore ethyl  $\beta$ -primeveroside. It is not thought to be formed

from primeverose during extraction (see Rabaté, Bull. Soc. Chim. biol. 1938, **20**, 449).

**Gaultherin** (see Monotropitin, p. 92a).

**Gein** (geoside),  $C_{24}H_{30}O_{11}, H_2O$ , m.p. 146°,  $[\alpha]_D -54^\circ$ , occurs in *Geum urbanum*. Hydrolysis by the enzyme gease gives vicianose (6- $\beta$ -*l*-arabinosido-*d*-glucose; cf. Vicianin, p. 97c) and eugenol (Vol. IV, 394d).



(Hérissey, Chem. Zentr. 1926, **I**, 2358; **II**, 2436; 1927, **1**, 1025).

**Genistin**,  $C_{21}H_{20}O_{10}$ , m.p. 254–256°,  $[\alpha]_D -28^\circ$ , is an isoflavone glucoside occurring with daidzin (v. *supra*) in *Soja hispida*. Acid hydrolysis gives *d*-glucose and genistein,  $C_{15}H_{10}O_6$ , m.p. 297–298°, which is 5:7:4'-trihydroxyisoflavone. The sugar in genistin is attached to position 7 (Walz, Annalen, 1931, **489**, 118). Genistein occurs also in dyer's broom, *Genista tinctoria* (Baker and Robinson, J.C.S. 1925, **127**, 1981; 1926, 2713; 1928, 3115).

**Gentianin** (*q.v.*).

**Geranyl-Glucoside**,  $C_{16}H_{26}O_8$ , m.p. 58°,  $[\alpha]_D -37^\circ$ , occurs in *Pelargonium odoratum*. It is a  $\beta$ -glucoside, which has been synthesised from the terpene geraniol (*q.v.*) and acetobromoglucose (Fischer and Helferich, Annalen, 1911, **383**, 77). It has also been obtained by enzymic synthesis, from geranol and *d*-glucose in the presence of emulsin (Bourquelot and Bridel, Compt. rend. 1913, **157**, 72; Chem. Zentr. 1913, **II**, 1309).

**Gesnerin** (*q.v.*).

**Gitalin** (v. Vol. II, 381c).

**Gitonin** is one of several saponins occurring (with cardiac glycosides) in the leaves of *Digitalis purpurea*, it is separated from digitonin by fractional precipitation with ether (Windaus, Z. physiol. Chem. 1925, **150**, 205), and also by fractional crystallisation from alcohol–water mixtures; it was first isolated by Windaus and Schneckenburger (Ber. 1913, **46**, 2628) from impure digitonin preparations. It has the probable molecular formula  $C_{51}H_{82}O_{23}$ , m.p. 272°. Hydrolysis gives galactose (2 mol.), an unidentified pentose (1 mol.) and a steroid gitogenin,  $C_{27}H_{44}O_4$ , m.p. 272°. The last compound has been assigned a structure closely similar to that of digitogenin (p. 87d) but having no hydroxyl group in position 6 (see Tschesche, Ber. 1935, **68** [B], 1090; Tschesche and Hagedorn, *ibid.* 1936, **69** [B], 797).

**Gitoxin**. A cardiac glycoside (v. Vol. II, 384b).

**Glucocheirolin**,  $C_{11}H_{20}O_{11}, S_3NK \cdot H_2O$ , m.p. 160°,  $[\alpha]_D -21.5^\circ$ , is a mustard-oil glucoside found in the seeds of wallflowers (*Cheiranthus cheiri*). It is hydrolysed by the enzyme myrosinase to cheirolin (Vol. II, 527c), *d*-glucose and potassium hydrogen sulphate (Schneider and

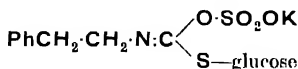


Lohmann, *ibid.* 1912, **45**, 2954; **46**, 2634; *see also* Annalen, 1912, **386**, 346) (*cf.* Singrin, p. 96a). A homologue of cheirolin, erysolin



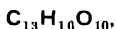
occurs as a glucoside in the seeds of the orange wallflower, *Erysimum perfolskianum*.

Gluc nasturtiin,  $\text{C}_{15}\text{H}_{20}\text{O}_8\text{S}_2\text{NK}$ , is a mustard-oil glucoside from the seeds of *Nasturtium officinale*. Hydrolysis by myrosinase gives *d*-glucose, phenylethyl isothiocyanate and potassium hydrogen sulphate (Gadamer, Ber. 1899, **32**, 2335) (*cf.* Singrin and Glucotropæolin).



Gluc nasturtiin

$\beta$ -Glucosido-Gallic Acid (Glucogallin),



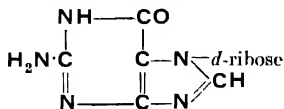
m.p. 193°,  $[\alpha]_D -21^\circ$ , is found in Chinese rhubarb (Fischer and Strauss, *ibid.* 1912, **45**, 3773; 1918, **51**, 1804) (*cf.* Tetram, p. 97a).

Glucotropæolin,  $\text{C}_{14}\text{H}_{16}\text{O}_8\text{S}_2\text{NK}$ , is a mustard-oil glucoside found in *Thrapis majus* and *Lepidium sativum*. Hydrolysis by the enzyme myrosinase gives *d*-glucose, benzyl isothiocyanate ( $\text{PhCH}_2\text{NCS}$ ), and potassium hydrogen sulphate (Gadamer, *l.c.*). It is therefore analogous to sinigrin and gluc nasturtiin.

Glycyphyllin,  $\text{C}_{21}\text{H}_{24}\text{O}_9\cdot 3\text{H}_2\text{O}$ , m.p. 175–180°, occurs in the leaves of *Smilax glycyphylla*; it appears to be a rhamnoside of phloretin (*see* Phloridzin, p. 93b) (Wright and Rennie, J.C.S. 1881, **39**, 237; Reunie, *ibid.*, 1886, **49**, 857).

Gossypitricin (*v.* Vol. III, 406b; *also* Neclakuntam and Seshadri, 1937, A., II, 445; 1939, A., II, 245).

Guanosine (Vernine) was the first nucleoside to be discovered in nature (Schulze and Bossard, Z. physiol. Chem. 1885, **9**, 448; 1886, **10**, 80). It occurs in various plant tissues (*Vicia*, *Lupinus*, etc.) and is a hydrolysis product of yeast-nucleic acid (*also* thymus- and pancreas-nucleic acids). It is 9-guanine-*d*-ribofuranoside, guanine being 2-amino-6-oxypurine (*see also*



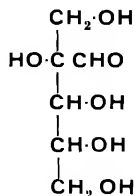
Levene and Jacobs, Ber. 1909, **42**, 2474; 1910, **43**, 3163; Gulland and Holaday, J.C.S. 1934, 1639; 1938, 692). Guanylic acid has a phosphoric acid residue in position 3 of the ribose, and it is in this form that guanosine occurs combined in the nucleic acids.

Gynocardin,  $\text{C}_{13}\text{H}_{10}\text{O}_9\text{N}$ , m.p. 163°,  $[\alpha]_D +72.5^\circ$ , is a cyanophoric glucoside found in the oleaginous seeds of *Gynocardia odorata*. It is accompanied by an enzyme, gynocardase, which hydrolyses it to *d*-glucose, hydrocyanic acid and a diketone of unknown structure (Power and Lees, J.C.S. 1905, **87**, 349; Brill, Chem. Zentr. 1923, I, 104; Floriana, *ibid.* 1929, I, 761).

Gypsophila-Saponin (alba-saponin, saponalbin) is a saponin belonging to the hederin group

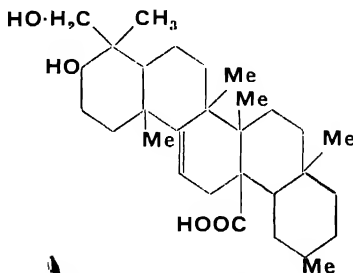
(*v. infra*). It occurs in *Gypsophila arrostii* and *paniculata* (Kofler and Dafert, *ibid.* 1924, I, 922). Hydrolysis gives arabinose, rhamnose, glucose, galactose and gypsogenin,  $\text{C}_{26}\text{H}_{44}\text{O}_8$ , which on dehydrogenation yields, among other products, sapotalin (1:2:7-trimethylnaphthalene) (Ruzicka *et al.*, Helv. Chim. Acta, 1932, **15**, 1496).

Hamamelitannin,  $\text{C}_{20}\text{H}_{20}\text{O}_{14}$ , m.p. 117°, occurs in *Hamamelis virginica* (Freudenberg and Blümmel, Annalen, 1924, **440**, 45). Hydrolysis by the enzyme tannase or by acids gives gallic acid (2 mol.) and a hexose, hamamelose (1 mol.), for which the following constitution has been proposed (Schmidt, *ibid.* 1929, **476**, 257).



Reduction of the corresponding aldonic acid with hydriodic acid gives methyl propyl acetic acid; hamamelose gives no osazone and has a slight laevo rotation. Identification is rendered difficult by the fact that the sugar has not yet been obtained crystalline. Freudenberg (*l.c.*) suggests that the gallic acid molecules are attached through their carboxyl groups to the primary alcoholic groups of the hexose.

Hederin belongs to a small group of triterpenoid saponins the aglycones of which are not of the sterol type (as in the case of digitalis saponins; *see* Digitonin, p. 87c) but appear to be triterpenoid in character. Their constitution is still under investigation. *Æscin*, camelia-saponin, caryocar-saponin, cyclamin, gypsophila-saponin, quillaja-saponin, etc., are of this class. Hederin ( $\alpha$ -hederin) is one of several saponins found in ivy (*Hedera helix*); others present have not yet been characterised as chemical individuals. It is crystalline, having the molecular formula  $\text{C}_{41}\text{H}_{64}\text{O}_{11}$ . Hydrolysis yields rhamnose, arabinose and hederagenin,  $\text{C}_{30}\text{H}_{48}\text{O}_8$ , m.p. 331°,  $[\alpha]_D +70^\circ$ . In common with the aglycones of other members of this group, hederagenin on dehydrogenation yields sapotalin (1:2:7-trimethylnaphthalene). A suggested structure for hederagenin is given below:



Hederagenin (provisional).

(Ruzicka *et al.*, *Helv. Chim. Acta*, 1937, **20**, 299, 325; 1938, **21**, 1371; *Z. Katsato, Acta Phytochim.* 1936-37, **9**, 43, 61, 75; 1937-38, **10**, 199). (See also Spring, *Chem. and Ind.* 1936, **55**, 964, 1050.)

**Helicin** (Spirain),  $C_{13}H_{16}O_7$ , m.p. 174-175°,  $[\alpha]_D -60^\circ$ , is salicylaldehyde- $\beta$ -glucoside. It occurs in *Spiraea* species and is formed when salicin is oxidised with nitric acid (Schiff, *Annalen*, 1870, **154**, 15). It has been synthesised from salicylaldehyde and acetochloroglucose (Michael, *J. Amer. Chem. Soc.* 1879, **1**, 305; *Ber.* 1879, **12**, 2260). Emulsin hydrolyses helicin and also its hydrazone and oxime.

**Hellebrin** is a crystalline cardiac glycoside (*v.* Vol. II, 387c).

**Hesperidin**,  $C_{28}H_{34}O_{15}$ , m.p. 251°, is a flavanone glycoside found in the peel of several *Citrus* fruits (not *Citrus decumana*) (Tiemann and Will, *Ber.* 1881, **14**, 948). Hydrolysis gives *d*-glucose, *L*-rhamnose and hesperitin,  $C_{16}H_{14}O_6$ , m.p. 228°, which is 5:7:3'-trihydroxy-4'-methoxyflavanone (synthesis: Shinoda and Kawagoye, *Chem. Zentr.* 1929, **1**, 244). The sugars appear to be present as a biose (King and Robertson, *J.C.S.* 1931, 1704).

**Hiptagin**,  $C_{16}H_{14}O_9N_2 \cdot \frac{1}{2}H_2O$ , m.p. 110°,  $[\alpha]_D +3.5^\circ$  (in acetone), is a cyanophoric glucoside found in the root bark of *Hiptage medabloti*. Dilute acid gives *d*-glucose and various degradation products; dilute alkali yields ammonia and hydrogen cyanide even in the cold. It is considered to be the glucoside of an isoxazole derivative (see Gorter, *Amer. Chem. Abstr.* 1921, **15**, 1299).

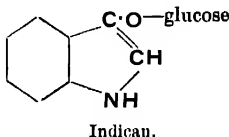
**Hirsutin** (*q.v.*).

**Hiviscin**,  $C_{26}H_{20}O_{16}Cl \cdot 3H_2O$  (chloride), is an anthocyanin obtained from *Hibiscus sabdariffa*, m.p. 178°. Hydrolysis gives glucose, a pentose and delphinidin chloride (see Delphinin) (Yamamoto and Osima, *Chem. Zentr.* 1933, **1**, 71; 1937, **A**, II, 71).

**Idæin**, (*q.v.*).

**Incarnatrin** is a flavonol glycoside, from *Trifolium incarnatum* (crimson clover). It is hydrolysed by emulsin to glucose and quercetin (see Quercetrin, p. 94c) (Rogerson, *J.C.S.* 1910, **97**, 1004).

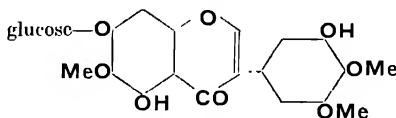
**Indican**,  $C_{14}H_{17}O_5N \cdot 3H_2O$ , m.p. 58° (anhyd. 178°),  $[\alpha]_D -77.6^\circ$ , occurs in various species of *Indigofera* and *Isatis tinctoria*, etc. It is  $\beta$ -indoxyl glucoside, being the form in which indigo occurs in the plant. Hydrolysis by the enzyme indemulsin (with which it is found) or by acids gives *d*-glucose and indoxyl, which is readily oxidised (*e.g.* by air) to indigotin.



Indican is hydrolysed slowly by emulsin. For the synthesis of indican, see Robertson, *J.C.S.* 1927, 1937; *ibid.* 1933, **30**. Indole derivatives are eliminated from the body in the form of indican.

**Inosinic Acid** is a purine nucleotide, and was first discovered in meat extract by Liebig in 1847. Careful hydrolysis gives phosphoric acid and inosine, 9-hypoxanthine-*d*-ribofuranoside. In inosinic acid the phosphoric acid residue is on position 6 of the sugar (Levene and Jacobs, *Ber.* 1908, **41**, 2703; 1909, **42**, 335; 1911, **44**, 746; Levene and Tipson, *J. Biol. Chem.* 1935, **111**, 313). In fresh tissues inosine is largely replaced by its precursor adenine-5-phosphoribofuranoside; the latter is transformed into inosinic acid by a specific enzyme. The position of the ribose side-chain is discussed by Gulland and Holiday (*J.C.S.* 1936, 765).

**Iridin**,  $C_{24}H_{26}O_{13} \cdot H_2O$ , m.p. 208° (anhydrous 217°), is an isoflavone glucoside found in the rhizomes of iris (*Iris florentina, germanica*, etc.). Acid hydrolysis yields *d*-glucose and irigenin,  $C_{18}H_{16}O_8$ , m.p. 186°, 5:7:3'-trihydroxy-6:4':5'-trimethoxyisoflavone (Baker, *ibid.* 1928, 1022). (*Cf.* Tectoridin, p. 96d.)

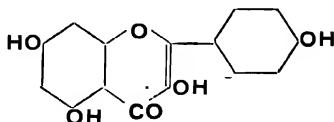


For the synthesis of iridin, see Baker and Robinson, *J.C.S.* 1929, 152.

**Jalapin** (scammonin, orizabin),  $C_{34}H_{62}O_{18}$ , m.p. 208°, is found in *Sipites jalapa*, *Convolvulus orizabensis* and *Scammonia*. Hydrolysis gives *d*-glucose, *L*-rhamnose, *d*-fucose (rhodose, *Vol. V*, 330c) and jalaponic acid,  $C_{16}H_{32}O_8$  (11-hydroxyhexadecanoic acid), m.p. 68° (Davies and Adams, *J. Amer. Chem. Soc.* 1928, **50**, 1749; Votoček and Valentin, *Amer. Chem. Abstr.* 1928, **22**, 1361) (*v.* *Convolvulus*).

Jalapin has a hemolytic effect similar to that of the saponins; it paralyses the motor parasympathetic nerves (Heinrich, *Biochem. Z.* 1918, **88**, 13; Hollander, *Amer. Chem. Abstr.* 1936, **30**, 5305).

**Kæmpferin**,  $C_{27}H_{30}O_{16}$ , m.p. 195°, is a flavonol glycoside found in senna leaves. Hydrolysis gives glucose (2 mol.) and kæmpferol (campherol), 5:7:4'-trihydroxyflavonol, m.p. 277° (Tutin, *J.C.S.* 1913, **103**, 2006).



Kæmpferol is the aglycone of several other glycosides (kæmpferitrin, robinin, etc.).

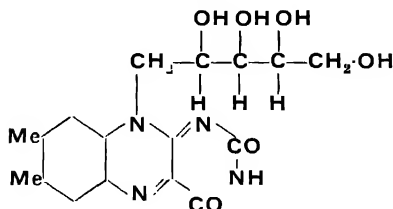
**Kæmpferitrin**,  $C_{27}H_{30}O_{14}$ , m.p. 203°, is a flavonol glycoside, found in Java indigo (*Indigofera arrecta*). Hydrolysis gives rhamnose (2 mol.) and kæmpferol (*v. supra*) (Tasaki, 1927, *A.*, 918). The rhamnose appears to be attached, as a disaccharide, to the hydroxyl group in position 3.

**Keracyanin** (Prunicyanin), *v.* Vol. I, p. 449a.

**Kerasin**,  $C_{48}H_{93}O_8N \cdot H_2O$ , m.p. 187°,  $[\alpha]_D -11.6^\circ$  ( $CHCl_3$ ), is a galactolipin occurring in

the brain (see Klenk and Harle, Z. physiol. Chem. 1930, **189**, 243; Chibnall, Piper and Williams, Biochem. J. 1936, **30**, 100).

**Lactoflavin** (now riboflavin, vitamin B<sub>2</sub>) 6:7-dimethyl-9-d-ribitylisoalloxazine, is necessary for the growth of rats (György, Kuhn and Wagner-Jauregg, Naturwiss. 1933, **21**, 560). For synthesis, see Karrer, Helv. Chim. Acta, 1935, **18**, 426, 522, 1435.



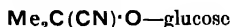
Lactoflavin.

It is interesting to note that the ribose may be eliminated by irradiation in neutral solution.

**Linamarin** (phaseolunatin),



m.p. 142°,  $[\alpha]_D -29^\circ$ , is a cyanophoric glucoside found in young flax (*Linum usitatissimum*) and in *Phaseolus latus* (Jorissen and Hairs, Bull. Acad. roy. Belg. 1891, **21**, 529). It occurs also in the rubber tree, *Hevea brasiliensis*. It is hydrolysed by aqueous alkali to ammonia and phaseolunatinic acid,  $\text{C}_{10}\text{H}_{16}\text{O}_6$ , which with dilute acid gives d-glucose and α-hydroxyisobutyric acid,  $\text{Me}_2\text{C}(\text{OH})\text{COOH}$ . The structure of linamarin is



(β-glucoside link). For synthesis, see Fischer and Anger, Ber. 1919, **52**, 854; Sitzungsber. K. Akad. Wiss. Berlin, 1918, 203. The action of enzymes upon linamarin has been the subject of contradictory reports. In general, it appears to be accompanied by a specific enzyme, *linase*, by which it is hydrolysed to d-glucose and acetone cyanhydrin. Emulsin yields d-glucose, acetone and hydrogen cyanide.

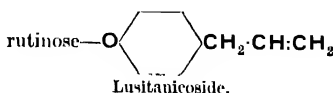
**Linarin**,  $\text{C}_{23}\text{H}_{24}\text{O}_{11}$ , is a flavone glycoside found in toad flax (*Linaria vulgaris*). Hydrolysis gives glucose, rhamnose and 6:4'-dimethylcutellarein,  $\text{C}_{17}\text{H}_{16}\text{O}_6$ , m.p. 218° (see p. 95d). (Schmid and Rumpel, Monatsh. 1932, **60**, 8; Merz and Wu, Amer. Chem. Abstr. 1936, 4166.)

**Liquiritin**,  $\text{C}_{21}\text{H}_{22}\text{O}_9$ , m.p. 212° (monohydrate) is a flavanone glycoside found in *Glycyrrhiza glabra* (*Radix liquiritiae*). Hydrolysis gives d-glucose and liquiritigenin, 7:4'-dihydroxyflavanone, m.p. 207°. The glucose is attached at position 4' (Shinoda and Ueda, Ber. 1934, **67** [B], 434).

**Lotusin**,  $\text{C}_{28}\text{H}_{31}\text{O}_{16}\text{N}$ , m.p. >300°, is a cyanophoric glycoside isolated from *Lotus arabicus* by Dunstan and Henry (Proc. Roy. Soc. 1900, **87**, 224; 1901, **68**, 374). Its structure is still uncertain. Hydrolysis gives d-glucose (2 mol.), hydrogen cyanide and lotoflavin,  $\text{C}_{18}\text{H}_{10}\text{O}_6$ , m.p. >200°, probably 5:7:2:4'-tetrahydroxyflavone (see Robinson and Venka-

taraman, J.C.S. 1929, 61; Cullinane, Algar and Ryan, Proc. Roy. Dub. Soc. 1928, **19**, 77). The cyanogen radical appears to be attached to the sugar groups (see, however, T. A. Henry, J.S.C.I. 1938, **57**, 248, where Dunstan and Henry's investigations are not supported).

**Lusitanicoside**,  $\text{C}_{21}\text{H}_{30}\text{O}_{10}$ , m.p. 188°,  $[\alpha]_D -74^\circ$ , is found in Portuguese cherry laurel leaves (*Cerasus lusitanica*). Hydrolysis gives p-allylphenol (chavicol), d-glucose and l-rhamnose (Hérissey and Laforest, Chem. Zentr. 1932, **II**, 232; 1934, **I**, 2137). The sugars are present as the biose rutinose (β-1-l-rhamnosido-6-d-glucose) and lusitanicoside is therefore chavicol-



β-rutinoside (synthesis. Zemplén and Gerecs, Ber. 1937, **70** [B], 1098).

**Luteic Acid** is a synthetic glycoside formed by the action of *Penicillium luteum* on d-glucose (Raistrick and Rintoul, Chem. Zentr. 1932, **I**, 1107). Hydrolysis yields d-glucose (2 mol.) and malonic acid (1 mol.). (See also Birkinshaw and Raistrick, Biochem. J. 1933, **27**, 370; Vol. V, 58a).

**Lycoperdin**,  $\text{C}_{13}\text{H}_{24}\text{O}_6\text{N}_2$ , is an amino-sugar glycoside found in lycoperdon. Hydrolysis gives glucosamine (2 mol.) and formic acid (1 mol.); it reduces Fehling's solution and gives the biuret reaction (Kotake and Sera, Z. physiol. Chem. 1913, **88**, 56).

(For the constitution of glucosamine, see Haworth, Lake and Pent, J.C.S. 1939, 271.)

**Malvin**,  $\text{C}_{28}\text{H}_{35}\text{O}_{11}\text{Cl}$  (chloride), is an anthocyanin present in the wild mallow, *Malva sylvestris* and in *Primula viscosa*. Hydrolysis gives glucose (2 mol.) and malvidin chloride,  $\text{C}_{17}\text{H}_{15}\text{O}_7\text{Cl}$ . The latter is sometimes called syringidin chloride, as degradation yields syringic acid (3:5-dimethoxygallic acid). Malvidin chloride is the 3':5'-dimethyl ether of delphinidin chloride (v. Vol. III, 554d). The glucose molecules are attached in positions 3 and 5 (Kondo, Chem. Zentr. 1930, **I**, 3193; Robinson and Robinson, Nature, 1931, **128**, 413). Malvin has been synthesised by Robinson *et al.* (J.C.S. 1932, 2299). Malvidin (also pelargonidin and peonidin) do not give colour reactions with ferric chloride and sodium acetate in amyl alcohol solution.

**Mecocyanin**,  $\text{C}_{27}\text{H}_{31}\text{O}_{15}\text{Cl}$  (chloride), is an anthocyanin present in the red poppy (*Papaver rhoeas*) (Willstätter and Weil, Annalen, 1917, **412**, 237; Robinson and Robinson, Nature, 1931, **128**, 413). It is cyanidin-3-gentiobioside (Grove, Inubuse and Robinson, J.C.S. 1934, 1608) and yields on hydrolysis glucose (2 mol.) and cyanidin chloride (see CYANIN).

**Melilotin** (melilotoside),  $\text{C}_{18}\text{H}_{15}\text{O}_8\text{H}_2\text{O}$ , m.p. 240-241°,  $[\alpha]_D +68^\circ$ , is found in the flowers of *Melilotus altissima* and *arvensis* (Charaux, Bull. Soc. Chim. biol. 1925, **7**, 1056). It is hydrolysed by emulsin (and acids) to glucose and o-coumaric acid.

**Methoxyapiin** is a flavone glycoside found with apin (q.v.) in parsley. Hydrolysis gives

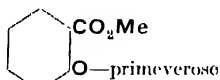
glucose (2 mol.) and methoxyapigenin (diosmetin), the 4'-methyl ether of luteolin (*see* Galuteolin, p. 88) (Von Gerichten, Ber. 1900, **33**, 2334; Annalen, 1901, **318**, 121).

**Methylarbutin**, *see* Arbutin, p. 30.

**Methylcichorin**, *see* Cichorin.

**Monardæin** (Salvinin),  $C_{36}H_{36}O_{17}Cl$  (chloride), is an anthocyanin present in *Monarda didyma* (Karrer and Widmer, Helv. Chim. Acta, 1927, **10**, 67, 729). Hydrolysis gives glucose (2 mol.), *p*-hydroxycinnamic acid, malonic acid and pelargonidin chloride (*see* Pelargonin, p. 93). It appears to be similar to salvinin (from *Salvia splendens*) (Karrer and Widmer, *ibid.* 1929, **12**, 292).

**Monotropitin** (Gaultherin, Monotropitoside)  $C_{10}H_{20}O_{12} \cdot H_2O$ , m.p. 92° (179.5° anhydrous)  $[\alpha]_D -57^\circ$ , is found in various species of *Gaultheria* and *Spiraea*. It is hydrolysed by the enzyme gaultherase (primeverase) to primeverose (6- $\beta$ -xylosidoglucose) (*v.* Vol. II, 300b) and methyl salicylate. Acid hydrolysis gives glucose, xylose and salicylic acid.



(*cf.* Salicin, Populin and Violutin).

Monotropitin has been synthesised (Robertson and Waters, J.C.S. 1931, 1881). Both glycosidic linkages are of the  $\beta$ -type.

**Morindin**, m.p. 245°, is an anthraquinone glycoside found in species of *Morinda*. Hydrolysis gives glucose (2 mol.) and morindone, 1:5:6-trihydroxy-2-methylanthraquinone (Simonsen, J.C.S. 1918, **113**, 766).

**Myricitrin**,  $C_{21}H_{20}O_{12}$ , m.p. 200°, found in the leaves of the *Rhus* species and in the bark of various *Myrica* species, is a flavonol rhamnoside. Hydrolysis gives rhamnose and myricetin,  $C_{15}H_{10}O_6$ , m.p. 360°, which is 5:7:3':4':5'-pentahydroxyflavonol (Nierenstein, Ber. 1928, **61** [B], 361; Hattori and Hayashi, Chem. Zentr., 1932, I, 2043).

**Myrticlorin** is identical with rutin (p. 95) (A. G. Perkin, J.C.S. 1910, **97**, 1776).

**Myrtillin**,  $C_{23}H_{23}O_{12}Cl$  (chloride), is an anthocyanin occurring in whortleberries (*Vaccinium myrtillus*, *see* Idain). Hydrolysis yields galactose (1 mol.) and myrtillidin chloride,  $C_{16}H_{13}O_7Cl$ , the 7-methyl ether of delphinidin chloride (*v.* Vol. III, 554d) (Willstätter and Zollinger, Annalen, 1915, **408**, 103; **412**, 204; Karrer and Widmer, Helv. Chim. Acta, 1927, **10**, 5).

**Naringin**,  $C_{27}H_{32}O_{14}$ , m.p. 171°,  $[\alpha]_D -84^\circ$ , is a flavanone glycoside found in the flowers and fruit of *Citrus decumana* (Will, Ber. 1885, **18**, 1311). Hydrolysis gives *d*-glucose, *L*-rhamnose and naringenin,  $C_{15}H_{12}O_5$ , m.p. 248°, 5:7:4'-trihydroxyflavanone (synthesis: K. W. and M. Rosenmund, Ber. 1928, **61** [B], 2608). Naringin is hydrolysed by an enzyme in celery seed to give naringenin and a disaccharide (Hall, Chem. and Ind. 1938, 473). It is the bitter principle of grapefruit (*see also* Zoller, Chem. Zentr. 1918, II, 635; Asahina and Inubuse,

Ber. 1928, **61** [B], 1514; Amer. Chem. Abstr. 1929, **23**, 3475).

**Nervon**,  $C_{48}H_{81}O_9N$ , m.p. 180°,  $[\alpha]_D -4.3^\circ$  (pyridine) and **hydroxynervon**,  $C_{48}H_{81}O_9N$ , occur in brain (*see* Klenk and Harle, Z. physiol. Chem. 1920, **189**, 243; Chibnall, Piper and Williams, Biochem. J., 1936, **30**, 100).

**Nodakenin**,  $C_{20}H_{24}O_9 \cdot H_2O$ , m.p. 216°,  $[\alpha]_D +57^\circ$ , occurs in *Peucedanum decursivum*. Hydrolysis gives *d*-glucose and nodakenetin,  $C_{14}H_{14}O_4$ , m.p. 185°,  $[\alpha]_D -22^\circ$ , which is a coumarin derivative of unknown constitution (Arima, Chem. Zentr. 1929, I, 1698; *ibid.* II, 753; Spath and Kainrath, Ber. 1936, **69** [B], 2062).

**Nucleic Acids**, which are found combined with proteins in the nucleus of plant and animal cells, have been found to contain sugars (especially *d*-ribose). Hydrolysis yields various fission products, including purine or pyrimidine glycosides (*e.g.* adenosine, cytidine, etc.). These are described under their own headings.

**Cenin**,  $C_{23}H_{25}O_{12}Cl$  (chloride), is an anthocyanin colouring matter of wine, occurring in *Vitis vinifera*. Hydrolysis yields glucose (1 mol.) and malvidin chloride,  $C_{17}H_{15}O_6Cl$ , (sometimes called cenidin or syringidin chloride) which is also obtained on hydrolysis of malvin (p. 91). The glucose is attached to the hydroxyl group in position 3 of malvidin chloride (Kondo, Chem. Zentr. 1930, I, 3193). Cenin has been synthesised by Robinson (J.C.S. 1931, 2701).

**Oleandrin** (Folnarin). A cardiac glycoside (*v.* Vol. II, 386b, c).

**Ononin**,  $C_{22}H_{22}O_9$ , m.p. 210°, is an isoflavone glycoside found in the roots of *Ononis spinosa* (Heumelmayer, Monatsh. 1902, **23**, 144; 1904, **25**, 555). It is the 4'-methyl ether of the glucoside daidzin (p. 87) (Wessely *et al.*, *ibid.* 1931, **57**, 395; Ber. 1933, **66** [B], 685; Monatsh. 1933, **63**, 201).

**Orobanchin** occurs in *Orobancha rapum*. Hydrolysis gives *d*-glucose, *L*-rhamnose and caffeic acid (Bridel and Charaux, Chem. Zentr. 1924, II, 850).

**Oroboside**, m.p. 220°,  $[\alpha]_D -61^\circ$  (pyridine), is a flavone glycoside present in *Orobos tuberosus*. It is hydrolysed by emulsin and is therefore a  $\beta$ -glycoside, the products being glucose and orobol, tetrahydroxyflavone (Bridel and Charaux, Compt. rend. 1930, **190**, 387).

**Osyritrin** is identical with rutin (p. 95) (A. G. Perkin, J.C.S. 1910, **97**, 1776).

**Ouabain**. A cardiac glycoside (*v.* Vol. II, 386a).

**Oxycoccicyanin**,  $C_{22}H_{23}O_{11}Cl$  (chloride), is an anthocyanin present in the fruit of *Oxycoccus macrocarpus* (American cranberries). Hydrolysis yields glucose (1 mol.) and pæonidin chloride (*vide infra*). The glucose is attached to the hydroxyl group in position 3 (Grove and Robinson, Chem. Zentr. 1932, II, 3252; Levy, Posternack and Robinson, J.C.S. 1931, 2715).

**Pæonin**,  $C_{25}H_{33}O_{16}Cl$  (chloride), m.p. 165°, is an anthocyanin which occurs in the red pæony (*Pæonia off.*). Hydrolysis gives glucose (2 mol.) and pæonidin chloride,  $C_{14}H_{13}O_6Cl$ , the 3'-methyl ether of cyanidin (in the type formula, hydroxyl groups in positions 3, 5, 7, 4'

$\text{OCH}_3$  in position 3'). The glucose molecules are attached to the hydroxyl groups in positions 3 and 5 (Nolan, Pratt and Robinson, *ibid.* 1926, 1936; Robinson and Robinson, *Nature*, 1931, 128, 413; Robinson and Todd, J.C.S. 1932, 1488; purification, Karrer and Strong, *Helv. Chim. Acta*, 1936, 19, 25).

**Pelargonin**,  $\text{C}_{27}\text{H}_{31}\text{O}_{15}\text{Cl}$  (chloride), m.p. 75–180°, is an anthocyanin pigment present in the scarlet pelargonium, orange dahlia and red cornflower. Hydrolysis gives glucose (2 mol.) and pelargonidin chloride,  $\text{C}_{15}\text{H}_{11}\text{O}_5\text{Cl}$ . The latter has hydroxyl groups in positions 3, 5, 7 and 4' in the type formula; the glucose molecules have been shown by synthesis to be attached to the hydroxyls in positions 3 and 5 (Robinson, *Nature*, 1936, 137, 94; Ber. 1934, 67 [A], 85). Pelargonin is therefore the 3:5 diglucoside of pelargonidin. Pelargonidin is the aglycone of other anthocyanins (*e.g.* callistephin).

**Periplocin** is a cardiac glycoside (*v.* Vol. II 386c).

**Periplocymarin** is a cardiac glycoside (*v.* Vol. II, 386a, d).

**Petunin**,  $\text{C}_{28}\text{H}_{35}\text{O}_{17}\text{Cl}$  (chloride), is an anthocyanin occurring in *Petunia hybrida*, m.p. 178°. Hydrolysis gives glucose (2 mol.) and petunidin chloride,  $\text{C}_{19}\text{H}_{13}\text{O}_7\text{Cl}$ , the 3'-methyl ether of delphinidin chloride. The sugars are probably attached to positions 3 and 5 (Bell and Robinson, J.C.S. 1934, 1604). Like delphinidin petunidin is rapidly destroyed by shaking with 10% aqueous caustic soda in the presence of air; most other anthocyanidins are stable. These two anthocyanidins are also distinguished from others of the group by remaining in the acid layer when partitioned between 1% aqueous hydrochloric acid and a mixture of cyclohexanol (1 vol.) and toluene (5 vol.) (Robinson *et al.*, *ibid.* 1930, 793; *Biochem. J.* 1931, 25, 1687).

**Pharbitic Acid**,  $\text{C}_{26}\text{H}_{46}\text{O}_{13}$ , occurs in the seeds of *Pharbitis nil*, m.p. 156–162°,  $[\alpha]_D -47^\circ$ . Acid hydrolysis gives glucose, rhamnose and ipuroic acid,  $\text{C}_{14}\text{H}_{26}\text{O}_4$ , 2:10-dihydroxymyristic acid,

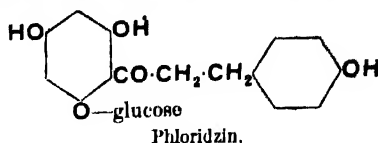


(Asalina *et al.*, J. Pharm. Soc. Japan, 1919, 452, 821; 1922, 479, 1; 1925, 520, 515).

It is interesting to note that in the blossoms of *Pharbitis nil* the glycosides present are anthocyanins (pelargonin, paeonin) (Kataoka, A., 1936, 1307).

**Phloridzin**,  $\text{C}_{21}\text{H}_{24}\text{O}_{10} \cdot 2\text{H}_2\text{O}$ , m.p. 109° (anhydrous, 171°),  $[\alpha]_D -50^\circ$ , occurs in the bark and root bark of many fruit trees (apple, pear, plum, cherry, and also in *Rosaceae* and *Ericaceae* (Bridel and Kramer, *Chem. Zentr.* 1932, I, 396) and in the leaves of *Kalmia latifolia* (*idem.*, *ibid.* 1933, II, 3289). There has been much contradictory evidence concerning the action of emulsin upon phloridzin (Moelwyn-Hughes, J. Gen. Physiol. 1930, 13, 807; Bridel, *Bull. Soc. Chim. biol.* 1930, 12, 921), the low solubility in water making the action difficult to detect with certainty. Hydrolysis by acid yields glucose and phloretin (*cf.* Glycyphyllin), m.p. 248°, a derivative of phloroglucinol (critical increment

for the hydrolysis, 22,920 g.-cal. see Moelwyn-Hughes, *Trans. Faraday Soc.* 1929, 26, 503).



For synthesis, see Fischer and Nouri, *Ber.* 1917, 50, 611. The position and pyranose structure of the sugar have been proved by methylation and hydrolysis (Müller and Robertson, *Chem. Zentr.* 1933, II, 3288). Injected internally in animals, phloridzin causes glycosuria; synthetic phloroglucinol- $\beta$ -glucoside is similar in its action.

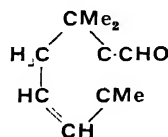
**Phrenosin** (cerebron), m.p. 212°,  $[\alpha]_D +8^\circ$  ( $\text{CHCl}_3$ ), a galactolipin occurring in brain and nerve material.

**Phyllanthin** is a cyanophoric glucoside found in the leaves of *Phyllanthus gassstroemi*. It is the glucoside of *p*-hydroxymandelonitrile (*cf.* Zuerin, p. 98). It is hydrolysed by emulsin (Finnemore, Reichard and Large, 1937, A., II, 136).

**Phytosterolin** (Gloriosol),  $\text{C}_{35}\text{H}_{60}\text{O}_6$ , m.p. 285–290°, is a glucoside of Phytosterol, a mixture of sterols. It occurs in the wheat germ and in other sources (Nakamura and Ichiba, *Chem. Zentr.* 1931, I, 3015) (*cf.* Sitosterolin, p. 96b, and Spinasterolin, p. 96c).

**Piceir**, **Picéoside** (Salinigrin, Ameliaroside, Salicinerin),  $\text{C}_{14}\text{H}_{18}\text{O}_7$ , m.p. 194°,  $[\alpha]_D -89^\circ$ , a glucoside in the bark of *Picea excelsa*, and *Salix discolor*. It is hydrolysed, by emulsin and by acids, to glucose and *p*-hydroxyacetophenone, m.p. 109° (Rabaté, *ibid.* 1930, II, 246; Jowett, J.C.S. 1932, 721). For synthesis, see Manthner, J. pr. Chem. 1913, [n], 88, 764.

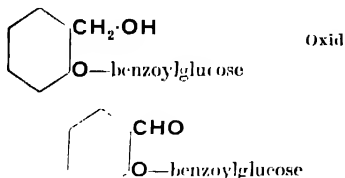
**Picrocrocin**,  $\text{C}_{16}\text{H}_{26}\text{O}_7$ , m.p. 166°,  $[\alpha]_D -58^\circ$ , is a terpene glucoside found in the *Crocus* species. Hydrolysis gives *d*-glucose and safranal (dehydro- $\beta$ -cyclocitral),  $\text{C}_{10}\text{H}_{14}\text{O}$ ,



(Kayser, *Ber.* 1884, 17, 2228; Winterstein, *Helv. Chim. Acta*, 1922, 5, 376; Lutz, *Biochem. Z.* 1930, 226, 97). The true aglucone appears to be hydroxy- $\beta$ -cyclocitral, and during hydrolysis a molecule of water is eliminated (Kuhn and Winterstein, *Ber.* 1934, 67 [B], 344). The glucosidic link is probably of the  $\beta$ -type and accounts for the low rotation. Its relation to the carotenoid plant pigments is interesting (*cf.* Vol. III, 429b).

**Populin**,  $\text{C}_{30}\text{H}_{42}\text{O}_8$ , benzoylsalicin, m.p. 180°,  $[\alpha]_D -53^\circ$ , is present in the bark of various species of poplar (*see* Salicin, p. 95a). Hydrolysis gives glucose, benzoic acid and saliginin (*o*-hydroxybenzyl alcohol). Oxidation gives benzoylhelicin; the benzoyl group must therefore

be attached to the sugar and not to the  $-\text{CH}_2\text{OH}$  group of salicin (cf. Monotropitin, p. 92a, and Violutin, p. 98a).



The benzoyl group appears to be attached to  $\text{C}_6$  on the glucose molecule (Richtmeyer and Yeckel, J. Amer. Chem. Soc. 1934, **56**, 2495).

Populin is not hydrolysed by emulsin, presumably owing to the presence of the benzoyl group. It has been reported that an enzyme from *Populus montifera* hydrolyses it to salicin and benzoic acid (Weevers, Proc. K. Akad. Wetensch. Amsterdam, 1909, **12**, 193) and taka-dias-tase to saligenin and  $\alpha$ -benzoylglucose (Kitsato, Biochem. Z. 1927, **190**, 109). It is hydrolysed completely by the bacteria in cheese.

Populin occurs in the petals of the Indian tulip, *Thespesia populnea* (Neelakantam and Seshadri, 1938, A., II, 394).

Primulaverin and Primeverin,  $\text{C}_{20}\text{H}_{26}\text{O}_{13}$ , are isomeric glycosides found in the roots of *Primula officinalis* (Goris and Mascré, Compt. rend. 1910, **149**, 947; Goris and Vischniac, Lc. 1919, **169**, 871). Primulaverin has m.p.  $160^\circ$ ,  $[\alpha]_D -67^\circ$ , and hydrolysis by the enzyme primaverase gives primoverose (see Monotropitin, p. 92a) and methyl 5-methoxysaheylate. Primeverin has m.p.  $203^\circ$ ,  $[\alpha]_D -71.5^\circ$  and gives on hydrolysis primeverose and methyl 4-methoxysaheylate (Jones and Robertson, J.C.S. 1933, 1618).

Proscillaridin A, a cardiac glycoside (v. Vol. II, 387a).

Prulaurasin, *dl*-mandelonitrile- $\beta$ -glucoside, m.p.  $123-125^\circ$ ,  $[\alpha]_D -53^\circ$ , is isolated from *Prunus laurocerasus* (Caldwell and Courtault, J.C.S. 1907, **91**, 671) and is also formed by partial hydrolysis of racemic amygdalin (*iso*amygdalin) (*q.v.*) by the enzyme prunase present in yeast (cf. Prunasin and Sambunigrin; see also Fischer and Bergmann, Ber. 1917, **50**, 1047).

Prunasin, *l*-mandelonitrile- $\beta$ -glucoside, m.p.  $148^\circ$ ,  $[\alpha]_D -27^\circ$ , occurs in *Prunus* species, in *Phytolacca serrulata* and *Eremophila maculata* (Power and Moore, J.C.S. 1910, **97**, 1099; Finnemore and Cox, Chem. Zentr. 1933, **1**, 1793). It is also formed by partial hydrolysis of amygdalin (*q.v.*) by the enzyme prunase, present in yeast and in emulsin (from bitter almonds). (See Fischer and Bergmann, Lc.)

Punicin, obtained from *Punica granatum*, appears to be identical with pelargonin (p. 93a) (Karrer and Widmer, Helv. Chim. Acta, 1927, **10**, 67).

Purpurea Glycoside A,  $\text{C}_{47}\text{H}_{74}\text{O}_{18}$ , is an amorphous cardiac glycoside obtained from the leaves of *Digitalis purpurea*. Enzymic hydrolysis gives digitoxin and glucose, while acid hydrolysis gives glucose (1 mol.), digitoxose (3 mol.) and the steroid digitoxigenin,  $\text{C}_{25}\text{H}_{34}\text{O}_4$ ,

m.p.  $250^\circ$  (Stoll and Kreis, Helv. Chim. Acta, 1935, **18**, 120; v. Vol. II, 385).

Purpurea Glycoside B,  $\text{C}_{47}\text{H}_{74}\text{O}_{19}$ , is a second amorphous cardiac glycoside obtained by Stoll and Kreis (*l.c.*) from the leaves of *Digitalis purpurea*. Enzymic hydrolysis gives gitoxin and glucose. Acid hydrolysis gives glucose (1 mol.), digitoxose (3 mol.) and the steroid gitoxigenin,  $\text{C}_{23}\text{H}_{34}\text{O}_5$ , m.p.  $235^\circ$  (cf. Purpurea Glycoside A, above).

Quercimeritrin,  $\text{C}_{21}\text{H}_{20}\text{O}_{12}$ , m.p.  $245^\circ$ , is a flavonol glycoside obtained from the flowers of Indian cotton (*Gossypium herbaceum*). Hydrolysis gives glucose and quercetin (*v. infra*) (A. G. Perkin, J.C.S. 1909, **95**, 2181). The sugar is attached to position 7 (Attree and Perkin, *ibid.* 1927, 234).

*iso*-Quercimeritrin is a flavonol glycoside which accompanies quercimeritrin in Indian cotton flowers. It is the 3- $\beta$ -glucoside of quercetin (Attree and Perkin, *l.c.*).

Quercitrin,  $\text{C}_{21}\text{H}_{20}\text{O}_{11}$ , m.p.  $176^\circ$ , is a flavonol glycoside found in oak bark (*Quercus tinctoria*), which is still used, after drying and grinding, as a dye for silk and wool. It occurs also in the horse-chestnut and in tea. Hydrolysis gives rhamnose and quercetin,  $\text{C}_{15}\text{H}_{10}\text{O}_7$ , 5:7:3':4'-tetrahydroxyflavonol, m.p.  $311^\circ$  (Asahina, Nakagame and Imubuse, Ber. 1929, **62** [B], 3016; J. pr. Chem. 1923, [ii], **106**, 1). Complete methylation of quercitrin by diazomethane, followed by hydrolysis of the sugar group, gives 5:7:3':4'-tetramethylflavonol; the sugar is therefore attached in position 3 (Attree and Perkin, *l.c.*).

Quillaia-Saponin,  $\text{C}_{35}\text{H}_{56}\text{O}_{12}$ , m.p.  $207^\circ$ , found in *Quillaia saponaria*, is of the hederin type (p. 89d) (Ruzicka *et al.*, Helv. Chim. Acta, 1932, **15**, 431). Hydrolysis yields glucuronic acid and quillaia saponogenin,  $\text{C}_{29}\text{H}_{46}\text{O}_5$ , m.p.  $294^\circ$  (Windaus, Chem. Zentr. 1926, **1**, 1815; Z. physiol. Chem. 1926, **160**, 301).

Rhamnazin,  $\text{C}_{23}\text{H}_{22}\text{O}_{12}$ , is a flavanol glycoside occurring with xanthorhamnin (p. 98a) in berries of the *Rhamnus* type. Hydrolysis gives glucose and rhamnazetin,  $\text{C}_{17}\text{H}_{14}\text{O}_7$ , 7:3'-dimethylquercetin, m.p.  $215^\circ$  (see Quercitrin) (Perkin and Martin, Chem. Zentr. 1897, **11**, 313; Perkin and Allison, *ibid.* 1900, **11**, 1243).

Rhamnicoside occurs in *Rhamnus cathartica*. It is a primeveroside (see Primulaverin) of pentahydroxy-2-methylantraquinone (Bridel and Charaux, Compt. rend. 1925, **180**, 1047, 1219; Ann. Chim. 1925, [x], **4**, 79).

Robinin (robinoside),  $\text{C}_{33}\text{H}_{40}\text{O}_{19}$ , m.p.  $197^\circ$ , is a flavonol glycoside from the flowers of *Robinia pseud-acacia*, in which acacium (*v. also*) also occurs, and in *Vinca minor*. Hydrolysis yields galactose (1 mol.), rhamnose (2 mol.) and kempferol (p. 90d). The sugars are present as a trisaccharide, robinose (Charaux, Bull. Soc. Chim. biol. 1926, **8**, 915; Chem. Zentr. 1932, **1**, 1908). Hydrolysis of robinin by enzymes gives kempferol and robinose. Other workers have isolated kempferol *l*-rhamnoside and a disaccharide, robinobiose, which is *l*-rhamnoside-*l*-galactose (Zemplén and Gerecs, Ber. 1935, **68**, [B], 2054).

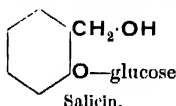
Ruberythric Acid,  $\text{C}_{35}\text{H}_{28}\text{O}_{13}$ , m.p.  $258-260^\circ$ , the anthraquinone glycoside, is 2- $\beta$ -prime-

verosido-alizarin (Jones and Robertson, J.C.S. 1933, 1167; Richter, *ibid.* 1936, 1701). It occurs in *Rubia tinctorum*.

**Rutin** (Sophorin, Osyritrin, Viola-quercitrin) is a flavonol glycoside found in *Ruta graveolens* and other plants; on hydrolysis it yields glucose, rhamnose and quercetin (p. 94c). The sugars are combined in the form of a biose, rutinose (obtained by enzymic hydrolysis), attached to the 3-hydroxyl group in quercetin. Rutinose is  $\beta$ -l-rhamnosido-6-d-glucose (Zemplén and Gerecs, Ber. 1935, 68 [B], 1318). (See also Attree and Perkin, J.C.S. 1927, 234.)

**Sakuranin**,  $C_{22}H_{24}O_{10}$ , m.p.  $212^{\circ}$ ,  $[\alpha]_D -106^{\circ}$ , is a flavanone glycoside found in the bark of the Japanese cherry (*Prunus yedensis*). Its constitution is not yet known; the aglycone is sakuranetin, 7-methylnaringenin (p. 92b) (Shinoda and Sato, Amer. Chem. Abstr. 1928, 22, 2947; 1929, 23, 2956).

**Salicin**,  $C_{13}H_{18}O_7$ , m.p.  $201^{\circ}$ ,  $[\alpha]_D -62.5^{\circ}$ , is found in willow bark (*Salix helix*) and other species of salix. Hydrolysis yields glucose and saligenin, o-hydroxybenzyl alcohol, m.p.  $86^{\circ}$ ; salicin is o-hydroxybenzyl- $\beta$ -glucoside (Piria, Ann. Chim. Pharm. 1845, 56, 35). Its benzoyl derivative, populin, occurs naturally (cf. also Monotropin and Violutin). It is hydrolysed by emulsin and also by a specific enzyme, salicase, found in the leaves and twigs of willows



(Sigmund, Monatsh. 1909, 30, 77). Salicin has long been used medicinally for fever and for rheumatism. The enzymic fission of salicin in heavy water has been studied by Steacie (Z. physikal. Chem. 1935, B, 28, 236). The rate of hydrolysis by acid has been measured by Moelwyn-Hughes (Trans. Faraday Soc. 1929, 25, 503).

**Salcinerin**, see Piccin (p. 93d).

**Salinigrin**, see Piccin (p. 93d).

**Salireposide**,  $C_{20}H_{22}O_8$ , m.p. anhyd.  $206^{\circ}$ ,  $[\alpha]_D -36.78^{\circ}$ , occurs in salix species. Hydrolysis gives d-glucose, benzoic acid and salirepol,  $C_7H_8O_3$ , probably 2:5-dihydroxybenzyl alcohol (Wattiez, Bull. Soc. Chim. biol. 1931, 13, 658; cf. Rabaté, *ibid.*, 1935, 17, 314).

**Salvinin**, see Monardein.

**Sambucin** is an anthocyanin occurring in elderberries (*Sambucus nigra*) and is apparently identical with chrysanthemin (q.v.) (Nolan and Casey, Amer. Chem. Abstr. 1932, 26, 497).

**Sambunigrin**, l-mandelonitrile- $\beta$ -glucoside, occurs in the leaves of *Sambucus nigra* (common elder) and *Acacia glaucescens* (Bourquetot and Danjou, Compt. rend. 1905, 141, 598; Finne-more and Cox, Chem. Zentr. 1930, I, 1806). The related compound, l-mandelonitrile- $\beta$ -gentiobioside (cf. Amygdalin), has not been found in nature (cf. Prunasin and Prulaurasin) (See Fischer and Bergmann, Ber. 1917, 50, 1047).

**Sapindus-Saponin** is found in *Sapindus mukorossi*, etc. (Winterstein and Meyer, Chem. Zentr. 1931, II, 1582; Kitsato and Sone, *ibid.* 1932, II, 1787). It is of the hederin type (q.v.).

**Saponarin**,  $C_{21}H_{34}O_{12} \cdot 2H_2O$ , m.p.  $236^{\circ}$ , is a flavonol glycoside occurring in the soap plant (*Saponaria* off.). Hydrolysis gives glucose and niterin,  $C_{15}H_{14}O_7$ , m.p.  $260^{\circ}$ , 6:7:4'-trihydroxy 2:3:6:7-tetrahydroflavonol (Barger, Ber. 1902, 35, 1296; J.C.S. 1906, 89, 1210).

**Sarmentocymarlin**. A cardiac glycoside (v. Vol. II, 386b). (See also Tschesche and Bohle, Ber. 1936, 69 [B], 2497.)

**Sarsaponin** (Parillin) is a saponin isolated from the Mexican sarsaparilla root. *Radix sarsaparillæ* (Jacobs and Simpson, J. Biol. Chem. 1934, 105, 501). The probable molecular formula of sarsaponin is  $C_{45}H_{74}O_{17}$ . Hydrolysis gives glucose (2 mol.), rhamnose (1 mol.) and a sterol, *Sarsapogenin* (parigenin),  $C_{27}H_{44}O_8$ , m.p.  $199^{\circ}$ . The last appears to differ from tigogenin (see Tigonin) only in the cis-trans relationship of the ring systems, but the structure is not yet definitely proved (see Simpson and Jacobs, J. Biol. Chem. 1935, 109, 573; 1935, 110, 565; Askew, Farmer and Kon, J.C.S. 1936, 1399; Farmer and Kon, *ibid.* 1937, 414).

**Scillaren A and B**. Carchac glycosides (v. Vol. II, 387a).

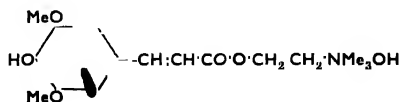
**Scopolin**,  $C_{22}H_{28}O_{14}$ , m.p.  $218^{\circ}$ , occurs, with methyl eichornin, in *Scopolia japonica*. Hydrolysis gives glucose (1 mol.) and *Scopoletin* 6-methoxy-7-hydroxy-coumarin (Seka and Kallir, Ber. 1931, 64, 909; Head and Robertson, Chem. Zentr. 1931, II, 851). The glucose is attached to position 7 (Merz, 1933, A, 72).



**Scutellarin**,  $C_{21}H_{18}O_{12}$ , m.p. above  $310^{\circ}$ , is a flavone glycoside occurring in the leaves of *Scutellaria baicalensis* and in the flowers of *Scutellaria altissima*. Hydrolysis gives glucuronic acid and *Scutellarein*, 4'-hydroxybaicalin. This is of interest in that baicalin occurs in the roots of *Scutellaria baicalensis*, joined to glucuronic acid (see Baicalin) (Robinson and Schwarzenbach, J.C.S. 1930, 822). Scutellarin is hydrolysed by baicalinase (Miwa, Amer. Chem. Abstr. 1932, 26, 4349).

**Serotrin**,  $C_{21}H_{20}O_{12} \cdot 3H_2O$ , has been described by Power and Moore (J.C.S. 1910, 87, 1099) as a flavonol glycoside present in *Prunus serotina* (wild black cherry). Hydrolysis yields glucose and quercetin.

**Sinalbin**,  $C_{30}H_{42}O_{15}S_2N_2 \cdot 5H_2O$ , m.p.  $84^{\circ}$  (anhyd.  $140^{\circ}$ ),  $[\alpha]_D -8^{\circ}$ , is a mustard-oil glucoside occurring in white mustard seed (*Sinapis alba*; cf. Sinigrin from *Sinapis nigra*). Hydrolysis by the enzyme myrosinase gives d-glucose, sinalbin mustard-oil (p-hydroxybenzyl isothiocyanate) and sinapin hydrogen sulphate. Sinapin is an ester of choline and sinapic acid.







bata and Ogawa, J. Pharm. Soc. Japan, 1928, 48, 1087; Mannich and Schumann, A. 1937, II, 276.

**Tetralin**,  $C_{32}H_{32}O_{12}$ , m.p.  $205^\circ$ , occurs in Chinese rhubarb (v.  $\beta$ -Glucosido-Gallic Acid). Hydrolysis gives *d*-glucose, cinnamic acid, gallic acid and rheosmin,  $C_{10}H_{12}O_2$ , m.p.  $79.5^\circ$ , of unknown constitution (Gilson, Chem. Zentr. 1903, I, 722).

**Thevetin**,  $C_{42}H_{66}O_{18}$ , is a cardiac glycoside found in the seeds of *Thevetia nerifolia* ("be-still nuts"). Hydrolysis appears to give glucose (2 mol.) and digitalose (1 mol.), and a sterol, *thevetigenin*,  $C_{23}H_{34}O_4$ , known only as the anhydro-compound, m.p.  $218-220^\circ$  (see Tschesche, Ber. 1936, 69 [B], 2368).

**Thymidine** is a pyrimidine nucleoside, obtained by hydrolysis of nucleic acids. It is 3-thymine deoxy-*d*-ribofuranoside (thymine is 2:4-dihydroxy-5-methylpyrimidine). Other deoxyribose nucleosides are known (see Deoxyadenosine) (Levene and Tipson, Science, 1935, 81, 98).

**Tigonin** is one of the several saponins which occur with cardiac glycosides in the leaves of *Digitalis purpurea*. The aglycone was isolated from this source by Jacobs and Fleck (J. Biol. Chem. 1930, 88, 545). The separation of the glycoside itself from the saponins with which it occurs (digitonin, gitonin, etc.) is very difficult; it is therefore fortunate that the only saponin in the leaves of *D. lanata* is tigonin, and purification is effected by means of its cholesterol addition product (Tschesche, Ber. 1936, 69 [B], 1665). Tigonin has probably the molecular formula  $C_{56}H_{92}O_{27}$ , m.p.  $260^\circ$ . Hydrolysis yields glucose (2 mol.), galactose (2 mol.), xylose (1 mol.) and a sterol, *tigogenin*,  $C_{27}H_{44}O_4$ , m.p.  $204^\circ$ . The last compound has been assigned a structure closely similar to that of digitonin (p. 87), but having no hydroxyl groups in positions 2 and 6 (see Tschesche, *loc. cit.*). It may be noted that one hydroxyl group (on  $C_1$ ) only is present and the position of attachment of the sugar residues is therefore established.

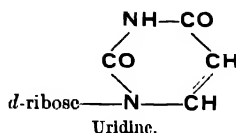
**Toringin**,  $C_{21}H_{20}O_9$ , is a flavone glycoside, m.p.  $240^\circ$ , isolated from *Pyrus toringo*. Hydrolysis gives glucose (1 mol.) and chrysin,  $C_{15}H_{10}O_4$ , 5:7-dihydroxyflavone, m.p.  $275^\circ$ , which occurs in the buds of several varieties of poplar (Piccard, Ber. 1873, 6, 884; Emulewicz, Kostanecki and Tambor, *ibid.* 1899, 32, 2448; Kostanecki and Lampe, *ibid.* 1904, 37, 3167).

**Typha-Glucoside**,  $C_{22}H_{32}O_{12}$ , is a flavonol glycoside found in *Typha angustata* and in the Indian dye Asbarg (*q.v.*). Hydrolysis gives glucose and *isorhamnetin*,  $C_{16}H_{12}O_6$ , 3'-methyl-quercetin, m.p.  $307^\circ$  (Fukuda, Chem. Zentr. 1928, I, 2100).

**Urechitin**, **Urechitoxin**. Crystalline cardiac glycosides (v. Vol. II, 387c).

**Uridine** is a pyrimidine glycoside (cf. Cytidine) formed by hydrolysis of yeast-nucleic acid. It is 3-uracil-*d*-ribofuranoside. In the nucleic acid, phosphoric acid is esterified in position 3 of the sugar. Pyrimidine glycosides are in general much more resistant to hydrolysis than purine glycosides (e.g. adenosine) and it is frequently necessary to hydrogenate before hydrolysis to obtain the sugar unchanged

(Levene and Tipson, J. Biol. Chem. 1934, 104, 385; 105, 419).

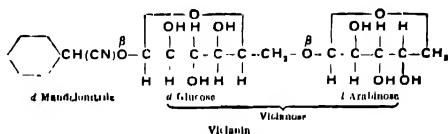


**Uzarin**. A cardiac glycoside (v. Vol. II, 386d).

**Vaccinin**,  $C_{15}H_{16}O_7$ ,  $[\alpha]_D +48^\circ$ , is obtained as a syrup from whortleberries (*Vaccinium vitis-idaea*). It is probably 6-benzoylglucose (Brigl and Zerrweck, Z. physiol. Chem. 1934, 229, 117); the benzoyl group is not in position 1, as vaccinin is reducing and forms a phenyl-hydrazone, but no osazone. Thus vaccinin is strictly not a glucoside, but an ester of glucose.

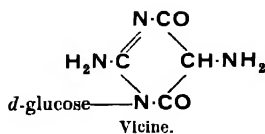
**Verbenalloside** (verbenalin),  $C_{17}H_{24}O_{10}$ , m.p.  $180^\circ$ ,  $[\alpha]_D -181^\circ$ , was first isolated from the flowers of *Verbena off.* (Bourdier, A. 1908, i, 197). Hydrolysis by emulsin or by dilute acid yields glucose and verbenalol,  $C_{11}H_{14}O_5$ , m.p.  $140.5^\circ$ ,  $[\alpha]_D -29^\circ$ , the structure of which is not yet known (see Cheymol, Bull. Soc. chim. 1938, [v], 5, 633).

**Vicianin**,  $C_{19}H_{26}O_{10}N$ , m.p.  $147-148^\circ$ ,  $[\alpha]_D -21^\circ$ , is a cyanophoric glycoside found in the seeds of wild vetch (*Vicia angustifolia*). It is accompanied by an enzyme, vicianase, by which it is hydrolysed to vicianose (a disaccharide), benzaldehyde and hydrogen cyanide. Vicianose is hydrolysed by acids and by emulsin to *d*-glucose and *L*-arabinose, and has been shown to be 6-( $\beta$ -*L*-arabinosido)-*d*-glucose (Helferich and Brederick, Annalen, 1928, 465, 166). Vicianin is therefore analogous to amygdalin (*q.v.*), one molecule of *d*-glucose being replaced by *L*-arabinose.



Vicianose occurs also in the glycosides Violuto-side and Gein (*q.v.v.*).

**Vicine**,  $C_{10}H_{18}N_4O_7$ , is 2:5-diamino-4:6-dioxypyrimidine glucoside, isolated from vetch seeds (together with convicine, p. 86d) by Ritthausen (J. pr. Chem. 1870, [ii], 2, 333). The structure below has been assigned by



Levene (J. Biol. Chem. 1914, 18, 305. See also *ibid.* 1916, 25, 607; Hérissay and Cheymol, Compt. rend. 1930, 191, 387; Bull. Soc. Chim. biol. 1931, 3, 29; Fisher and Johnson, J. Amer. Chem. Soc. 1932, 54, 2038).

of purines (Échevin and Brunel, *Compt. rend.* 1937, **205**, 294; Mouroi, *ibid.* 1938, **207**, 407); as an intermediate product in the deamination of glycine (H. Barrenscheen and Danzer, *Z. physiol. Chem.* 1933, **220**, 57; Abderhalden and Baertich, *Fermentforsch.* 1937, **15**, 342); by the activation of oxalic acid (Schroer, *Ber.* 1936, **69** [B], 2037; Weber and Režek, *Ber.* 1937, **70** [B], 407); and by the action of moulds on  $(\text{AcO})_2\text{Ca}$  and  $\text{AcONa}$  (Bernhauer and Scheuer, *Biochem. Z.* 1932, **253**, 11).

Glyoxylic acid may be prepared by heating 1 part dibromosuccinic acid with 8-10 parts water for 24 hours at  $140^\circ$  (Grimaux, *Compt. rend.* 1876, **73**, 63; Cramer, *Ber.* 1892, **25**, 714). For preparation of the anhydrous acid, see Talvitie, *Amer. Chem. Abstr.* 1936, **30**, 434.

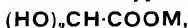
The acid is manufactured from sodium chloroacetate (Mugdan and Wimmer, *G.P.* 672481).

**Physical Properties.**—Glyoxylic acid is a viscid syrup with a suffocating smell; it crystallises by long standing above  $\text{H}_2\text{SO}_4$  forming rhombic prisms of composition

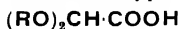


(Perkin, *Ber.* 1875, **8**, 188; Debus, *J.C.S.* 1904, **85**, 1390; Böttinger, *Arch. Pharm.* 1891, **232**, 68), extremely hygroscopic and easily soluble in water (Debus, *Annalen*, 1856, **100**, 11). Electrolytic dissociation const.  $k_{25} = 0.474 \times 10^{-3}$  (Ostwald, *Z. physikal. Chem.* 1889, **3**, 188). For quantitative electrolytic oxidation of glyoxylic acid, see A. Talvitie, *Ann. Acad. Sci. Fennica*, 1936, **A**, **45**, No. 6, 32.

**Chemical Properties.**—Decomposes on heating above its melting-point first into glycollic acid, oxalic acid and water vapour (Debus, *J.C.S.* 1904, **85**, 1391). It is a tautomeric substance; it exhibits aldehyde properties in condensing with hydroxylamine, phenylhydrazine, and semicarbazide (Elbers, *Annalen*, 1885, **227**, 353; Fischer, *Ber.* 1884, **17**, 576; Simon and Chavanne, *Compt. rend.* 1906, **143**, 904), but most of its salts are of the type



whilst dialkyl ethers of the type



have been prepared. It is oxidised to oxalic acid by  $\text{HNO}_3$  (Adler, *exp. Path. Pharm.* 1907, **56**, 210); by aqueous bromine solution (Debus, *Annalen*, 1863, **126**, 152); by silver oxide (Debus, *ibid.* 1856, **100**, 6); and, together with glycollic acid, by  $\text{KOH}$  (Böttinger, *Ber.* 1880, **13**, 1932).  $\text{KMnO}_4$  oxidises glyoxylic acid in alkaline solution to oxalic acid and  $\text{CO}_2$  (Evans and Adkins, *J. Amer. Chem. Soc.* 1919, **41**, 1407). Oxidised by  $\text{H}_2\text{O}_2$  in alkaline solution to  $\text{CO}_2$  and  $\text{H}\cdot\text{COOH}$  (Heimrod and Levene, *Biochem. Z.* 1910, **29**, 46). Reduction with zinc in aqueous solution yields glycollic acid; in acetic solution, tartaric acid (Genvresse, *Compt. rend.* 1892, **114**, 555). In the presence of  $\text{Ag}_2\text{O}$ ,  $\text{H}_2\text{S}$  yields thioglycollic acid with other products (Böttinger, *Annalen*, 1879, **198**, 213). With  $\text{HCN}$  it forms a cyanhydrin which, on hydrolysis, yields tartaric acid;  $\text{NaHSO}_3$  yields a crystalline compound (Debus, *ibid.* 1856, **100**, 5). It condenses with

urea to form allantoin and with guanidine to form in the cold glyoxylic guanidide and on warming to  $100^\circ$  iminoallantoin (Doebner and Gärtner, *ibid.* 1901, **315**, 1; 1901, **317**, 157; Simon and Chavanne, *Compt. rend.* 1906, **143**, 51; Kaess and Gruszkiewicz, *Ber.* 1902, **35**, 3604). For other condensation products, see Böttinger, *Arch. Pharm.* 1894, **232**, 549, 704; 1895, **233**, 100, 199; Bougault, *Compt. rend.* 1909, **148**, 1270; Griesheim, *Frdl.* II, 647; Wöchster, *Frdl.* X, 588.

**Detection.**—Glyoxylic acid may be identified even in dilute solution by precipitation of di-xanthyldiazone-glyoxylic acid,



with xanthidol and hydrazine hydrate in acetic acid (Fosse and Hiculle, *Compt. rend.* 1925, **181**, 286). The acid also yields an intense magenta red colour with Schryver's reagent (Fosse and Hiculle, *ibid.* 1924, **179**, 636). For descriptions of the substituted phenylhydrazones, see Chattaway and Bennett, *J.C.S.* 1927, 2850; Chattaway and Dalby, *ibid.* 1928, 2756. Glyoxylic acid may be titrated with alkali, or with permanganate in the presence of  $\text{H}_2\text{SO}_4$  (Hatcher and Holden, *Trans. Roy. Soc. Canada*, 1925, [iii], **19**, III, 11). For colour reaction with indole derivatives, see Gränström, *Beitr. Chem. Physiol. Path.* 1908, **11**, 132.

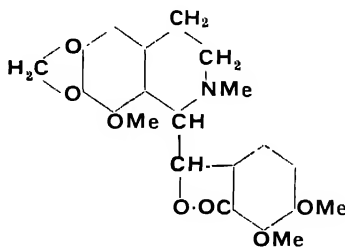
**Microchemical Detection.**—Behrens (*Chem.-Ztg.* 1902, **26**, 1128).

**GLYPHENARSINE** (v. Vol. I, 487b).

"GLYPTALS" (v. Vol. II, 472d).

**GMELINOL**,  $\text{C}_{12}\text{H}_{14}\text{O}_4$ . The white deposit in the cells of *Gmelina leichhardtii* (Colonial Beech). Gmelinol contains two methoxyl groups present as in veratric acid, and yields a mono-acetyl derivative (Smith, *J. Roy. Sci. N.S. Wales*, 1913, **46**, 187). It melts at  $122^\circ$  and on cooling solidifies to a transparent resin-like solid which melts at  $62-63^\circ$ , but when powdered has melting-point  $120-121^\circ$ .

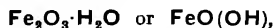
**GNOSCOPINE**, *dl*-narcotine,



occurs in opium and is formed by racemising narcotine. It forms colourless needles, m.p.  $229^\circ$ ; *picrate*, m.p.  $188-189^\circ$ ; *methiodide dihydrate*, prisms, m.p.  $210-212^\circ$ . For synthesis and resolution, see Perkin and Robinson, *J.C.S.* 1911, **99**, 775.

**GOA POWDER** (v. Vol. I, 457b).

**GOETHITE** (named after the poet Goethe). Hydrated ferric oxide,



crystallised in the orthorhombic system and isomorphous with the corresponding aluminium

and manganese minerals diaspore and manganite. It is included with limonite under the term "*brown iron-ore*," and when fibrous and massive the two are not readily distinguished, especially as they have the same colour and streak. Goethite, however, contains more iron ( $\text{Fe}_2\text{O}_3$  89.9, Fe 62.9%) and less water (10.1%) than limonite ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). Although limonite is sometimes fibrous and crystalline, it is never found as distinct crystals; crystals of goethite, however, are not uncommon. They are prismatic, acicular, platy or scaly in habit, and have a perfect cleavage in one direction (parallel to the brachy-pinacoid). Reniform and stalactitic masses with a radiating fibrous structure also occur. Sp.gr. 4.0-4.4, of crystals 4-37; hardness 5  $\frac{1}{2}$ . The colour is yellowish-brown to brownish-black, with usually a brilliant lustre on crystal-faces. Thin crystals and splinters are blood-red by transmitted light. The colour of the streak or powder is yellowish-brown. Analyses often show the presence of small amounts of manganese oxide and silica. Several varieties are distinguished. The acicular forms, usually with a radial grouping, are known as *needle iron-ore*. The needles may be very fine and closely packed together, giving the appearance of plush, as in *summetblende* or *summeterz* (velvet-ore) also known as *prizbramit*, from Przibram in Bohemia. *Ouegite* is acicular goethite embedded in amethyst from Lake Ouega, Russia. This material is cut as a gemstone under the name "Cupid's darts" (*flèches d'amour*). As an enclosure in other gem-minerals goethite is found in aventurine (*q.v.*) and sunstone. *Mesabite* is an ochreous variety abundant amongst the iron ores of the Mesabi Range in the Lake Superior district of Minnesota. The modes of occurrence of goethite are the same as for limonite, and it is present in many limonitic iron ores. Fine groups of crystals were formerly obtained in abundance in the Restormel iron mines at Lanlivery and in the Botallack mine at St. Just in Cornwall. Larger, but less perfect, crystals are known from the Pike's Peak district in Colorado.

Scaly forms of  $\text{FeO}(\text{OH})$  include lepidocrocite and pyrrhosiderite (or rubinglimmer), which until recently were regarded as varieties of goethite. These are also orthorhombic, but they differ from the acicular goethite in their optical properties and in their crystal structure as determined by X-rays; and they are now included under the distinct species lepidocrocite, which is dimorphous with goethite and isomorphous with boehmite (*q.v.*). Diaspore, isomorphous with goethite, is a fourth member of this isodimorphous series. The dimensions of the unit cells are:

	$\text{FeO}(\text{OH})$		$\text{AlO}(\text{OH})$
Goethite	$\left\{ \begin{array}{l} a \ 4.54\text{\AA} \\ b \ 10.0\text{\AA} \\ c \ 3.03\text{\AA} \end{array} \right.$	Diaspore	$\left\{ \begin{array}{l} a \ 4.40\text{\AA} \\ b \ 9.39\text{\AA} \\ c \ 2.84\text{\AA} \end{array} \right.$
Lepidocrocite	$\left\{ \begin{array}{l} a \ 3.87\text{\AA} \\ b \ 12.51\text{\AA} \\ c \ 3.06\text{\AA} \end{array} \right.$	Boehmite	$\left\{ \begin{array}{l} a \ 3.78\text{\AA} \\ b \ 11.8\text{\AA} \\ c \ 2.85\text{\AA} \end{array} \right.$

**GOLD.** Au (Aurum). At. wt. 197.2, at. no. 79.

**Historical.**—Gold cannot have escaped the observation of the men of the Stone Age, but it could have been of little use to them until they had discovered the art of melting. Flint daggers with gilt handles have been found in Egypt, and gold was well known in that country about 3,600 B.C., when its value in relation to silver was fixed by law. It was first used for coinage in Lydia, about 700 B.C., in the form of electrum, a native alloy of gold and silver.

The earliest method of obtaining gold, other than that of collecting it by hand, was by gravity concentration. The auriferous sand was stirred in a shallow stream of water running over sloping rocks, the heavy grains of gold settling to the bottom. Sheep-skins were spread out for entangling the particles of metal and helping in its collection. Over 2,000 years ago, the methods of ore-crushing by stone hammers and also by means of grinding mills were adopted in Egypt to release gold contained in solid rock. The powdered ore was washed on sloping tables (Gowland, J. Roy. Anth. Inst. 1912, 42, 256). The use of sieves to separate the insufficiently crushed pieces of rock is also attributed to the Egyptians. Stamp batteries for crushing ore were established at Joachimsthal in 1519, and sieves set at the outlet of the mortars were described by Agricola in 1556.

The use of mercury for separating gold from other materials, by amalgamation, was described by Pliny, and referred to by Theophilus in the eleventh century in his description of the extraction of gold from the sands of the Rhine. The method used in the Tyrol of stirring crushed ore with large quantities of mercury in circular bowls is very old, but the practice of charging mercury together with uncrushed ore into the mortars of stamp batteries, and catching the gold amalgam on copper plates was not mentioned before 1850.

The cyanide process was invented by MacArthur and Forrest in 1847, and flotation was first applied to a gold ore in 1900 (J. S. Elmore, Trans. Inst. Min. Met. 1900, 8, 379) although little success was obtained until much later. The methods of refining gold by the cementation process and by cupellation are very ancient. Nitric acid for refining was in use in Venice in the fifteenth century and was not superseded by sulphuric acid until the nineteenth century. The electrolytic refining process was invented in 1888, and the chlorine process of refining in 1867.

**Gold Ores.**—Gold is widely distributed in nature and occurs in minute traces in many ores of other metals. It has been detected in igneous and metamorphic rocks in almost every case in which a careful search for it has been made, and sedimentary rocks are seldom quite free from it. The comparatively small quantities of gold in limestones which have been formed in clear water far from land, appear to indicate the land as the place of origin of the gold, but it is also present in sea water.

Gold occurs in quantities large enough to pay for extraction in many quartz veins or lodes in rock formations. The gold is disseminated in

the quartz and is accompanied by brown oxides of iron in the upper portions of the deposits and by sulphides in the deep-seated portions. It usually occurs as native gold, mainly because its compounds are easily reduced. Even when it is contained in pyrites or other sulphides, it is present in the free state. Native gold also occurs in many secondary or detrital ("placer") deposits, such as river gravels, sea beaches, etc., in the form of nuggets, grains and flakes. The auriferous beds of conglomerate in the Transvaal are generally considered to be of this character.

Nuggets show crystalline structure when polished and etched, but rarely exhibit regular crystal faces or angles externally. Native gold always contains some silver and copper, and other metals are usually present in smaller proportions.

Telluride of gold is found in large quantities in Western Australia, Colorado and Transylvania, and has been reported from many other localities. There is only one true compound of gold and tellurium,  $\text{AuTe}_2$ , which contains 43.6% of gold; but several mixtures consisting of various compounds of tellurium with gold and silver and other metals have been recognised as mineral species. The best known of these are (1) *calaverite* (*q.v.*), which has the composition  $\text{AuTe}_2$ , (2) *sylvanite* or graphitic tellurium which is supposed to correspond to  $(\text{Au}, \text{Ag})\text{Te}_2$ , (3) *petzite*, a telluride of silver,  $\text{Ag}_2\text{Te}$ , with part of the silver replaced by gold, and (4) *nagayagite* or foliated tellurium, which contains some lead.

Auriferous telluride is usually dark grey or black in colour, but occasionally is silver-grey. Sometimes it contains an admixture of metallic gold which gives it a brassy-yellow colour. It is soft and brittle but its density is high, usually between 8 and 9. When heated in air, it oxidises, fuming and giving off  $\text{TeO}_2$ , and fuses below a red heat. If the roasting process is continued, most of the tellurium is removed and the gold is left in the form of spherical pellets which have solidified from fusion. Calaverite may contain as much as 44% of gold, but usually partly replaced by silver. A specimen of sylvanite from Cripple Creek, Colorado, contained **Aw** 7.64%, **Ag** 32.39%, **Te** 59.96% (F. C. Smith, Trans. Amer. Inst. Min. Met. Eng. 1897, **26**, 485).

**Extraction of Gold from its Ores.**—The metallurgical treatment of gold ores is usually simple and cheap and owing to this circumstance and to the high value of the metal, ores containing very small proportions of gold can be worked at a profit. Thus the ores of the Witwatersrand, now being worked, usually contain less than 0.001% gold, and auriferous gravels, which do not require crushing, may be worked when considerably poorer.

**Washing Auriferous Gravel** (*see* U.S. Bureau of Mines Information Circular No. 6786, 1934).—The gold occurring in placers is obtained by washing away the lighter gravel from the gold disseminated through it, the material being carried by a shallow stream of water through inclined troughs (sluice-boxes) or over sloping tables. The heavy particles of gold sink to the bottom of the stream and are caught by the rough surface of blanketing or plush, or in crevices which are formed by the

supply of "riffles" of various kinds. Sometimes the riffles consist of wooden strips or poles, sometimes of iron rails or sheets of "expanded" metal. Mercury is sprinkled in the stream and accumulates in the crevices, where it assists in catching the gold as an amalgam. The gold-amalgam, recovered in the periodical "clean-up," is strained through canvas to remove the excess of mercury and afterwards retorted.

The gravel is mined in various ways, according to circumstances. It may be raised by the spade and thrown into the stream, or, when in high banks, it may be broken down and washed away by jets of water (hydraulic mining). Dredgers are largely used to recover the gravel from river beds and also on dry alluvial "flats." In the latter case, the dredger floats in a pond, and travels slowly across country, scooping away the ground in front and stacking it behind after it has been washed. The gravel is usually washed on the deck of the dredger and the gold may be further concentrated by flotation. For descriptions of modern dredgers, *see* Eng. and Min. J. 1934, **135**, 486, and 1935, **136**, 270. Placer mining is now of less relative importance than formerly owing to the exhaustion of many of the known deposits.

**Ore Crushing.**—Ore from lodes and other compacted material is treated by crushing, followed by (1) Amalgamation, (2) Cyaniding, or (3) Concentration, either by gravity or by flotation. A combination or succession of two or more of these processes is usually employed. The object of crushing is to free the particles of gold and thus facilitate their separation from the gangue or remainder of the ore. Many different crushing machines are used. The stamp battery (*see* Caldecott and others, "Rand Metallurgical Practice," Vol. 1, 1926, Vol. II, 1919, C. Griffin), evolved from the pestle and mortar, was first applied to the industry early in the sixteenth century and is still in wide use. In modern practice it consists of heavy iron or steel stampers, ranging up to about 2,000 lb. in weight, which are raised and let fall in mortars kept supplied with ore and water. The height of drop is usually about 7 or 8 in. and the number of drops per minute about 100. Five stamps, ranged in line in a mortar, form a unit, and a battery may consist of any number of units. Wire mesh screens or steel plates perforated with holes are placed in the side of the mortar through which the wet pulp is discharged. The screens were formerly of comparatively fine mesh, *e.g.* 40 holes to the linear inch (coarser screens are used now to increase output), and the finely crushed ore was passed directly to amalgamation or concentration tables. Amalgamation tables consisted of sloping copper plates on which mercury had been spread by scrubbing until it formed a completely amalgamated surface. A thin stream of pulp, often mixed with mercury which had been fed into the mortar, flowed over the plates, on which the gold amalgam was caught and retained and subsequently removed by rubbers or scrapers and retorted. Much finely divided gold usually escaped the plates, remaining with the pulp (now "tailings") which went to the cyanide plant. These practices have been discarded in general, as mentioned later.

Ore from mines, however, contains material too coarse for crushing by stamps, and this is separated beforehand by means of a "grizzly" (iron bars in parallel) or by a vibrating screen of say 3 in. mesh. The coarse material is crushed in rock-breakers to 3 in. size before going to the stamps. Jaw crushers with reciprocating motion (hinged plates opening and closing successively) and gyratory crushers are both used. The latter, such as the Gates, Newhouse and Symons cone crushers, contain vertical revolving spindles set eccentrically to the outer casing and crush the ore between surfaces on the spindle and casing. These machines are of great capacity and besides being used to feed stamps, Symons cone crushers, for example, may take their place, ore being reduced to a maximum size of  $\frac{1}{4}$ -inch with crushers worked in series.

Fine crushing by stamps, previously mentioned, is no longer the common practice. It has been superseded by more gradual reduction in successive machines. Coarser screens are used with modern heavy stamps, giving a product of  $\frac{1}{2}$  in. to 1 in. in diameter. The stamp duty has become much higher and may be over 20 tons per stamp per day. In one instance (Prentice, *Trans. Inst. Min. Met.* 1935, **44**, 479) 45 tons of Rand ore were crushed per day through a screen of 1 in. mesh with a single Nissen stamp of 1,910 lb. Each Nissen stamp (Nissen, *J. Chem. Met. Soc. S. Africa*, 1911, **12**, 111) has its own cylindrical mortar box with a large screen area. The product of such work is too coarse for amalgamation and is passed to some form of grinding machine.

Tube mills are much used for fine grinding. They consist of revolving horizontal cylinders, half-filled with large pebbles, steel balls or pieces of hard ore, by the impact and abrading effect of which, in falling, coarse particles of sand are finely crushed. The pulp enters through one trunnion and passes out through the other which is fitted with a grid plate to retain the pebbles in the mill while allowing both sand and slime to pass out. The water in the pulp fed to tube mills is carefully regulated. There must be enough to make the particles of ore adhere to the pebbles but no "free" water. For Rand ores the usual proportion of water is 24–32% of the feed. The pulp coming from primary crushing machines usually passes through classifiers (described later) which remove both slimed ore and excess water, leaving clean wet sand to enter the tube mills. The product from the mills contains much material which is insufficiently crushed. This is separated from the fines by means of classifiers and returned to the tube mill ("closed circuit grinding"). The finished product will pass through a screen of about 90 or 100 mesh.

Among other fine grinders are (1) the Hardinge conical ball mill (*Trans. Amer. Inst. Min. Met. Eng.* 1908, **39**, 336) in which a pear-shaped grinding chamber replaces the cylinder of the tube mill (the change of design is to obviate further grinding of ore already fine enough), (2) the Marey ball mill, (3) the Marey rod mill, in which steel rods, 2 or 3 in. in diameter and a few inches shorter than the mill, are used instead of balls or pebbles for crushing. In small-scale

operations in outlying gold-fields, e.g. in Rhodesia, the Hardinge ball mill sometimes takes the place of stamps instead of being used in conjunction with them.

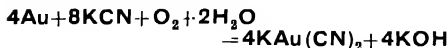
Classifiers are in wide use for separating sand from slime in pulp coming from tube mills. The earliest forms were inverted pyramids, which were superseded by inverted cones (Caldecott, *J. Chem. Met. Soc. S. Africa*, 1909, **9**, 312), the pulp entering at the centre from above and the fine stuff overflowing at the periphery. The sand settles in the cone and passes through a spigot at the apex. A stream of clear water is introduced near the apex of the cone in many instances and, rising through the sand, cleans it to some extent and overflows at the top with the slime. The spigot product or "underflow" is returned to the tube mill. Cone classifiers, however, are of comparatively small capacity and are now little used on the Rand, where they were introduced, except as de-waterers. The Dorr classifier has taken their place on many mines. It consists of an inclined rectangular trough, open at the upper end. The pulp enters on a transverse line about half way down the trough. The sand settles in the pulp and is pushed up the inclined bottom of the trough by a series of rakes which are lifted and lowered at opposite ends of their stroke. The sand presently emerges from the liquid and is then washed and discharged from the open upper end of the machine with about 26% of moisture. The slime is prevented from settling by the flow of the liquid and by the agitation caused by the reciprocating scrapers. It overflows the dam at the lower end of the machine.

The Dorr bowl classifier consists in the addition of a shallow circular bowl, with revolving rakes, to the ordinary rake classifier. The pulp enters near the centre and the slime overflows at the periphery of the bowl, while the sand settles to the bottom and is raked to a central discharge opening, whence it passes to the reciprocating rake compartment for further treatment before being returned to the tube mills.

*Gravity Concentration.*—The use of tube mills in a "closed circuit" with classifiers results in an "all-slimed" product, the sand going round the circuit until it has been sufficiently reduced to pass to the cyanide plant. Such fine grinding, however, is not required for gravity concentration, which can deal with unclassified pulp coming from stamp batteries fitted with 50 or 60 mesh screens, as at Morro Velho (J. H. French and H. Jones, *Trans. Inst. Min. Met.* 1933, **42**, 189), or from stamps with  $\frac{1}{2}$ -in. screens, followed by a single passage through a tube mill, as in some mines on the Rand. The ancient method of catching gold on roughened sloping surfaces was for a long period of time modified by adding mercury to the pulp and thus amalgamating the gold. This particular use of mercury is, however, being gradually abandoned. Amalgamation tables are becoming obsolete and have been widely superseded by blanket strakes (*cf.* Jason's Golden Fleece). These consist of strips of blanketing, canvas or more recently corduroy, stretched over sloping tables, with an inclination of  $1\frac{1}{2}$ –2 in. per ft. The pulp flows over them in a thin stream of uniform depth. No

mercury is used and the particles of gold, sinking to the bottom, adhere to the rough fibres of the corduroy or lodge against its ribs. The tailings pass to the cyanide circuit. The corduroy is removed and washed when necessary, usually every few hours. The concentrates thus obtained are fed to shaking concentration-tables such as the Wilfley table or the James table. (For description of these tables, see Rose and Newman, "Metallurgy of Gold," 1937, pp. 241 and 243.) In these, a number of strips of wood placed transversely are nailed on the surface to act as riffles. They retain the heavy particles which work to one edge of the table under the influence of a slight but rapid shake. The light worthless material is carried away by the water. (At Morro Velho, Brazil, the substitution of James tables for canvas strakes was completed in 1935, with improved results.) The concentrates are then ground and amalgamated in iron or steel revolving barrels containing steel balls, water and mercury. The amalgam is strained in canvas bags to remove excess mercury and retorted. Blanket recoveries on the Rand are from 25 to 60% of the gold in the ore, bringing this portion more quickly to account than if cyanide were used alone for treatment (Prentice, Trans. Inst. Min. Met. 1935, 44, 479).

**The Cyanide Process.**—The tailings from amalgamation plates or from blanket strakes or other concentrators contain some finely divided gold which is usually readily soluble in solutions of the cyanides of the alkali metals (v. Vol. III, 486b). Crushed virgin ore is also treated by cyaniding. The cyanide used at first was impure potassium cyanide, then mixtures of potassium and sodium cyanide and later sodium cyanide. Calcium cyanide containing an equivalent of 49% NaCN is also in use. It is still common practice to refer to the standard of these cyanides in terms of the potassium salt. Thus 97–98% NaCN is designated as 129–130% cyanide or potassium cyanide. The solvent action of cyanide on gold is very slow and requires the presence of an oxidising agent such as free oxygen. It may be expressed by the following equation, which represents the sum of the chemical actions:—



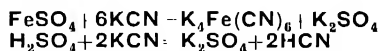
(J. S. MacLaurin, J.C.S. 1893, 63, 724). The equation, however, ignores galvanic action and subsidiary chemical changes which may have an important influence on industrial extraction (Allen, Trans. Amer. Inst. Min. Met. Eng. 1934, 112, 546).

The potassium aurocyanide remains dissolved in the water. The oxygen required is dissolved in the cyanide solutions from the air in contact with them. If the oxygen is exhausted owing, for example, to the cyanide solutions remaining for some time in contact with ore containing readily oxidisable sulphides or organic matter, dissolution of the gold is stopped, and it is necessary to aerate the pulp. Very dilute solutions of cyanide are used, containing from about 0.5% to as little as 0.001% of potassium cyanide. The maximum solution rate is at about 0.027%

KCN, when saturated with oxygen (H. A. White, J. Chem. Met. Soc. S. Africa, 1919, 20, 1; see also White, *ibid.* 1934, 35, 1). With Rand ores, the maximum strength in treating sands is 0.06% KCN and for slimes, solutions containing 0.01 to 0.025% KCN are used (Prentice, Trans. Inst. Min. Met. 1935, 44, 511).

In practice the solution rate depends mainly on the amount of oxygen dissolved in the solution. In a mass of ore undergoing treatment it is difficult to maintain a sufficient quantity of oxygen in a free state. Hence the time required for treatment may be many hours or even days, although under favourable conditions the gold could be dissolved in a few minutes or at most in 2 or 3 hours. Various oxidising methods have been applied, such as the passage of a current of air through the charge or agitation with air, or, more rarely, the addition of oxidisers other than air. The gold contained in sulphides is more difficult to dissolve than free gold, partly owing to oxygen deficiency, and rich sulphides are generally separated and treated in other ways.

Another difficulty in cyaniding lies in the waste of cyanide due to its destruction by certain constituents of the ore. Some sulphides and arsenides dissolve in cyanide and interfere with the efficiency of the solution. Moreover when pyrite, pyrrhotite or marcasite has been subjected to the action of air and water (weathering) before treatment, compounds are formed which are more prejudicial to the solution than the sulphides. The same decomposition occurs during treatment, especially in prolonged aeration and agitation. Ferrous sulphate and sulphuric acid are formed and react as follows:



Many other reactions occur, some copper and zinc minerals being especially troublesome cyanicides. Certain cupriferosous ores destroy so much cyanide that they cannot be treated profitably by the process.

The effect of acidity and of ferrous sulphate are overcome by the presence of sufficient protective alkali in the solution. This is provided by the addition of lime to the ore as it is fed to the battery, or at any grinding stage. The amount may be 2 or 3 lb. per ton. The protective alkali is kept as low as possible consistent with a reasonable consumption of cyanide (Robertson, *ibid.* 1924, 34, [i], 84) as an excess of lime may be fatal to extraction (Wright, *ibid.* 1933, 42, 230). Alkali does not protect cyanide from copper salts.

Crushed ore or tailings from other extraction processes are treated in large vats (containing as much as 850 tons of ore) with false bottoms provided with filter beds. Cyanide solution is run on to the ore and allowed to percolate through it. Fresh solution is added from time to time and finally the ore is washed with water. The solutions pass through the filter by which they are clarified and are conveyed to the precipitation boxes, where the gold is separated, as described later.

There are numerous modifications in the

cyanide process necessitated by the conditions or introduced as improvements. Of these, the variations in mechanical treatment are the most important and complex. Liquids do not pass readily through unclassified pulp, which is accordingly separated into sand and slime in classifiers, already described, or is merely run into a large vat filled with water. Here the sand settles and fills the vat and the slime is carried off in the overflow. The separation is, however, far from perfect. Either the sand is cyanided where it settles, or it is drained and transferred to another vat for the purpose, thus becoming well mixed and aerated. A solution of lead nitrate, to remove soluble sulphides, is sprinkled on the charge before it is removed to the treatment vat. On the Rand, the strong solution, containing from 0.05 to 0.1% KCN is run on to sand charges first, followed by weak solutions containing 0.02 or 0.03% KCN, and finally by wash water. As frequently as possible during the process, which lasts from 4 to 7 days, the sand is permitted to drain to allow the entry of air. In some instances vacuum pumps are used to expedite leaching and to assist aeration. The tailings are removed by sluicing or shovelling. They contain about 0.25 or 0.3 dwt. gold per ton or about 10% of that present in the sand before cyaniding, but part of the gold originally present has previously been caught on the blanket strikes. A large proportion of the residual gold is contained in the pyrites. The gold in the tailings could be further reduced in amount by finer grinding but it would not be profitable to do so. A product just fine enough to pass through a 100-mesh screen is aimed at.

The treatment of slime is becoming the most important part of the cyanide process. In *all-sliming* methods, the sand is reground until it can be included with the slime, so that no separate treatment is required. In many cases the gold is not completely laid open to attack until the ore is ground to slime and the recognition of this fact has led to a wide adoption of the *all-sliming* policy.

In practice the product of *all-sliming* operations usually contains from 5 to 35% of sand that will not pass a 200-mesh sieve. The slime, whether it is the portion separated from sand by classifiers or is the product of *all sliming*, is suspended in 5 to 10 parts of water and must be thickened before it can be cyanided. In order to promote its settlement a solution of lime is added, usually before or during grinding. The alkalinity is maintained at 0.002-0.025% CaO. This causes agglomeration or flocculation of the particles, "clouds of large and indefinite diameter are formed" and subside in the liquid. Heat assists settlement. With an alkalinity of not more than 0.005%, Rand slime settles at the rate of 2-4 ft. per hour with a clear overflow. The thickened slime contains only 35-45% moisture. The gold in it is readily dissolved by cyanide and the solution is separated from the slime either by decantation or filtration.

In the decantation method (Caldecott, "Rand Metallurgical Practice," 1926, Vol. I, p. 217), now little used, the settled slime is discharged from the settling vat by a jet of cyanide solution and pumped into another vat with a conical

bottom. Circulation is continued by withdrawing the pulp at the bottom and discharging it in oblique jets at the top. As soon as the gold is dissolved, which may be in from 4 to 24 hours, the pumps are stopped, the pulp allowed to settle, and the clear supernatant liquid is drawn off and sent to the precipitation plant. The pulp is diluted with "precipitated solution" to its original volume, agitated in a second vat, again allowed to settle and the liquor decanted. The settled slime, still containing about one-sixteenth of the dissolved gold, then goes to waste. (The Rand slime generally contains 2 or 3 dwts. gold per ton.) In counter-current lecanation, the cyanide solution enters at the bottom of the vat and overflows as a clear liquid at the top, the settlement of the slime generally more than keeping pace with the upward movement of the solution. The underflow of slime passes to another vat, and the action is continuous.

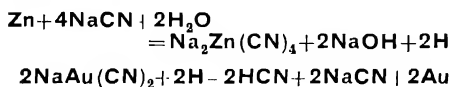
Slime is now generally treated by agitation with cyanide and filtration, with many variations in detail. The slime is first de-watered or thickened by settlement. The continuous thickeners now in common use, of which the Dorr machine is the best known, have scrapers attached to rotating radial arms which move the settled slime towards the centre of the vat, where it is discharged through a pipe. Pulp enters the vat at the centre and clear liquor over-flows at the periphery, the action being continuous in both cases. The thickened pulp is then agitated with cyanide solution in an "air-lift" machine such as the Brown or Pachuca tank. This consists of a tall cylinder of steel with a conical bottom. Inside the cylinder a central pipe is fixed extending nearly to the bottom and top. Air is forced into the central pipe near its lower end, and, bubbling up through the column of pulp inside it, reduces the density of the column. The pressure of the outside pulp on the open lower end of the pipe causes the column to rise and overflow at the top. Fresh pulp enters at the bottom of the pipe and a perfect circulation results, as well as complete aeration. The tank can be worked intermittently, being discharged as soon as the gold is dissolved, but in some Rand plants a series of agitators work continuously, each overflowing into the next, and the last delivering a finished product to gravitate to the filter plant (Thurlow and Prentice, J. Chem. Met. Soc. S. Africa, 1928, 28, 258).

The Brown tank agitators are confined to the treatment of 150-mesh or finer material, if building-up of coarse particles at the bottom is to be avoided. Coarser material or flotation concentrates may be treated in a Wallace agitator in which the air-lifts are assisted by a rotating impeller (S. G. Turrell, Chem. Eng. Min. Rev. 1934, 26, 312). This can deal with sand of 40 mesh.

The ore slime from the agitators, after being thickened by the removal of part of the liquid in raking machines, is filtered through canvas with the aid of a vacuum (as in the Moore, Butters, Oliver and other filters) or by direct pressure (as in the Merrill and Dehne filter presses). The liquid passes through leaving the solid matter as a cake adhering to the canvas.

The difficulty is that even a thin layer of slime packs down and offers great resistance to the passage of liquids. In practice, layers of  $\frac{1}{4}$ -1 in. are allowed to build up with vacuum leaching and layers of 2-3 in. with pressures of 40-100 lb. per sq. in. given by pumps. An enormous area of filtering surface is required in operations on a large scale. This is obtained by using a number of parallel vertical filter plates or leaves placed near together and kept separate by wooden strips or perforated iron plates or wire screens. The filter leaves may be contained in a basket which is immersed in the pulp and then lifted out for washing and discharge (Moore filter), or they may be fixed in a vat which is alternately filled with and emptied of pulp (Butters filter). Continuous filtration is arranged in some later machines (e.g. the Oliver and Dorco filters) by placing the filter leaves on the outside surface of a rotating drum which is partly immersed in the pulp. Filtration, washing and discharge of the slime cakes are then effected during each revolution of the drum. For details of some of these machines, see Rose and Newman, "Metallurgy of Gold," O. Griffin, 1937, pp. 357-369. The results are superior to those of the decantation method. For instance, Prentice (Trans. Inst. Min. Met. 1935, **44**, 517) states that the loss of dissolved gold in the residue from a vacuum filtration plant on the Rand was 0.022 dw. per ton of slime and that from a decantation plant 0.071 dw.

The recovery of gold from cyanide solutions is effected by precipitation with zinc shavings or zinc dust. The solutions, which may be turbid from suspended slimed ore, are clarified by passing them through beds of sand or preliminary filters before precipitation. It is believed that the actual precipitant is nascent hydrogen produced by the dissolution of zinc, thus:



Free hydrogen is, however, inert and if formed is removed as fast as possible. Precipitation is aided by coating the zinc with lead by means of a solution of lead nitrate, the lead-zinc couple increasing the rate of dissolution of the zinc. An excess of free cyanide is also favourable and it is usual to add cyanide to weak solutions on their way to the zinc boxes. Dissolved oxygen is detrimental by checking precipitation and wasting zinc, the solution is therefore de-aerated in modern practice. Oxygen is removed either by a vacuum (Merrill-Crowe process) or chemically. The former is the more efficient, and is installed in many modern plant. A vacuum of 22 in. of mercury is maintained in a large cylinder fitted with filter leaves, having a capacity in one plant of 6,000 tons of solution in 24 hours (Wartenweiler, J. Chem. Met. Soc. S. Africa, 1932, **32**, 143). The oxygen content is reduced from 6.0 to 0.5 mg. per litre. The chemical method involves the use of finely divided iron and highly pyritic sand in the clarifiers, or else the addition of manganese sulphate or tannin extract.

Zinc shavings when used are contained in long boxes divided into compartments through which the solution flows. The gold is precipitated in the form of black slime. In cleaning-up, the zinc is washed free from cyanide and the unbroken shavings are put back in the boxes. The gold slimes are digested in sulphuric acid or sodium bisulphate solution until all action has ceased. The residue, now freed from zinc, is washed, dried and fused in pots or tilting furnaces with borax, manganese dioxide, sodium carbonate and sand. After casting, the bullion is separated from the slag and sold to refineries. An alternative method is to smelt the precipitate with litharge, charcoal and fluxes, and to cupel the base lead-bullion produced (Taverner process). In modern practice precipitation is usually effected with zinc dust which is mixed with the clear cyanide solution in a tank fitted with vacuum filter-leaves (Merrill-Crowe process). The amount of zinc consumed is much less than when zinc shavings are used. The gold precipitate is washed off the filter leaves with jets of water and is sometimes smelted without previous acid treatment. Attempts to precipitate gold with finely ground charcoal instead of zinc have not had much success in practice. In recent years methods of regenerating the cyanide in spent liquors have been adopted on some mines. Sulphurous acid is added and the hydrocyanic acid thus formed is absorbed by lime (Halvorsen process, Min. and Met. 1925, **6**, 136; Mills-Crowe process, Lawr, Eng. and Min. J. 1929, **128**, 688).

The treatment of sulpho-telluride ores by cyanide presents special difficulties, as  $\text{NaCN}$  acts very slowly on these ores. Either the ore is roasted in order to expel the tellurium before cyaniding, as at Cripple Creek, Colorado and elsewhere (U.S. Bur. Mines, Information Circular 1933, No. 6739), or an addition of bromocyanide is made to ordinary cyanide, as at some mines in Western Australia and Canada (O'Malley, Chem. Eng. Min. Rev. 1933, **26**, 115). Bromocyanide readily dissolves telluride of gold. The bromocyanide is usually made in contact with the ore, as at Kirkland Lake, Ontario (J. T. Wiley, Eng. and Min. J. 1928, **126**, 16). Here the concentrates are stirred with 0.05% cyanide solution, and then  $\text{NaCN}$ , "Dow's salts" (a mixture of  $\text{NaBr}$  and  $\text{NaBrO}_3$ ) and  $\text{H}_2\text{SO}_4$  are added. Bromine is liberated by the action of the acid on Dow's salts and reacts with the  $\text{NaCN}$  forming bromocyanide (*v. Vol. III*, 504c).

Sometimes telluride ores are roasted before treatment with bromocyanide (A. James, *ibid.* 1927, **124**, 1004). Gold ores containing antimony as stibnite are also refractory, the stibnite dissolving in caustic alkali and decomposing cyanide. Roasting is useless unless the temperature is kept as low as  $450^\circ$ . At higher temperatures antimonates are formed, locking up the gold and protecting it against attack by cyanide. Long weathering of slimed ore containing stibnite makes it amenable to cyaniding (V. E. Robinson, J. Chem. Met. Soc. S. Africa, 1921, **21**, 117). The graphite in West African schist precipitates gold from aurocyanide but the difficulty in treating these ores is overcome by roasting before cyaniding (A. James, *l.c.*).



**Flotation (q.v.).**—This method of concentration is the most recent development of importance in the treatment of gold ores. In flotation the finely ground ore is mixed with water, air and less than 1% of oil, the ratio of water to solid being usually 3 or 4 to 1. The oil coats the particles of gold and minerals rich in gold and enables globules of air to adhere to them, so that they float to the top in a permanent froth which is skimmed off. The gangue particles are wetted by water and sink to the bottom. Besides oil, a number of other compounds are used in froth flotation, with various objects in view. Pine oil and cresol are in common use to form the froth, which must be stable enough to last while it is being removed from the machine. The amounts required vary from 0.05 to 0.15 lb. per ton of ore for pine oil and 0.1–0.5 lb. per ton for cresylic acid. "Collecting agents" such as xanthates, thiocarbamide and cresyl phosphate ("aerofloat") are used to enable the free gold and auriferous minerals to be floated, the amounts required being of the order of 0.1–0.3 lb. per ton. They are used in conjunction with "activators," such as copper sulphate and sodium sulphide, which assist in this action on some minerals. Copper sulphate and xanthates, however, cannot be used together as they form insoluble copper xanthate which is inactive. Sodium sulphide is advantageous in the presence of oxidised minerals such as copper carbonate and iron oxide, and in ores in which the gold is mixed with pyrite. "Modifiers" such as lime and soda ash assist in the wetting of the gangue particles, thus causing them to sink; they also neutralize acidity. Lime in excess, however, acts as a "depressor," causing both free gold and pyrite to sink. Sodium cyanide also acts as a depressor. "Dispersion agents" such as sulphuric acid and lime cause the gangue particles to separate from the mineral particles.

In flotation machines, the pulp and air entering a cell together are violently agitated by means of a central shaft fitted with blades or other form of impeller and revolving at high velocity (200–500 or more revolutions per minute). The impeller usually drives the pulp upwards and the air bubbles coated with mineral float to the surface and are scraped over the side of the vessel by revolving paddles. Among machines used in treating gold ores are the Minerals Separation subaeration, the Denver subaeration, the Fagergren and the Krant flotation machines. Several units or cells are used in series, so that the froth from the first cell may be treated again in "cleaner cells," and the gangue tailings in other cells. The whole series forms the "flotation circuit." The froth or concentrate containing the free gold and valuable minerals is usually sold to smelters, or treated by cyanidation.

Flotation supplements, rather than supplants, the older processes. It is recognised that there is an advantage in withdrawing as much gold as possible from the pulp at the earliest practicable stage of treatment, as may be done by flotation or gravity concentration. Free gold floats alone in the absence of sulphides (Richards and Locke, Min. Ind. 1932, 41, 590). Thus on a rich Californian ore a froth assaying some £2,700 per ton

with 60% extraction could be obtained by using only small quantities of "pentasol" xanthate and other reagents. The addition of two drops of pine oil per ton increased the assay value of the concentrates to £5,000 per ton. With some ores flotation is followed by cyanidation of the tailings, with others the cyanide treatment comes first. The tailings from amalgamation are also subjected to flotation in some instances.

There has been a rapid increase in the application of flotation to gold since the change from acid to alkaline circuits and from oils to synthetic organic chemical reagents. The alkalinity generally used is very slight, the  $p_H$  value (logarithm of the reciprocal of the hydrogen-ion concentration) of the pulp ranging from 7.0 to 7.5, the neutral figure being 7.0. Flotation is in use at many mines in the Kirkland old field Canada, in Western America, in West Australia and other countries. It is also being tried on the Rand on a large scale.

**Smelting.**—Gold ores containing appreciable quantities of lead or copper are usually smelted for the production of these metals, from which the gold is subsequently extracted. Other gold ores are sometimes useful as fluxes in the smelting operations (*v. COPPER*).

**Refining.**—Gold extracted from ores is usually impure and unfit for use in the arts until it has been refined. Preliminary refining or "toughening" operations are often carried out either at the refineries or at the gold mills before the bullion is sold. Sometimes the gold is melted in crucibles with oxidising agents such as nitre, or a blast of air is directed on the surface of the molten metal or even passed through it. The base metals are oxidised and form a dross which is skimmed off with the help of bone ash, or borax is added to form a fusible slag with the oxides of the metals. Toughened bullion contains little except gold, silver and copper.

**Refining by Sulphuric Acid.**—In this process, an alloy of gold and silver is prepared by melting gold bullion with *doré silver* (*i.e.* silver containing small quantities of gold) or Mexican dollars or, occasionally, with refined silver if no other is available. The parting alloy usually contains from 20 to 30% of gold and a few per cent. of copper. If a higher proportion of gold is present, some silver remains undissolved and is retained by the gold. The copper assists the dissolution of the silver but the amount of base metals present in the alloy is carefully regulated, as their sulphates are sparingly soluble in concentrated sulphuric acid and consequently are precipitated and interfere with the progress of the operation. Not more than 10% copper and 5% lead are allowed. A small quantity of lead is said to assist in the dissolution of copper.

The alloy is granulated by being poured into water while still molten and the granulations are boiled in concentrated sulphuric acid of *sp.gr.* 1.85 in cast-iron kettles. The amount of acid used is four or five times the weight of the granulations, but only about half this amount is added at first. The sulphur dioxide, which is formed in large quantities, is carried away through leaden pipes. Silver sulphate is retained in solution in the hot concentrated acid, but tends to be precipitated when the acid is

cooled or diluted. When the evolution of sulphur dioxide is at an end, the liquid is transferred to a settling pot, and fresh acid added. After three boilings in acid, the "brown gold" residue is washed with boiling water, dried, melted with nitre and cast in open moulds into ingots of about 400 oz. each.

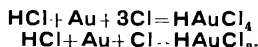
The acid solution of silver is poured into large lead lined tanks containing hot water and sheet or scrap copper, and is heated by means of steam and stirred until the precipitation of the silver is complete. The silver precipitate is washed, dried and compressed into cakes by hydraulic power before being melted. The copper is recovered by electro-deposition or as copper sulphate by crystallisation. The gold produced by sulphuric acid parting is usually from 996 to 999 fine, and the precipitated silver is about 996 to 998 fine.

*Refining by Electrolytic Deposition.*—In the United States, and in some refineries elsewhere, gold is refined by electrolysis. Two processes are used successively. In the *Mochius process*, a parting alloy containing about 30% of gold and 65-70% of silver, copper, lead, etc., including not more than 15% of base metals, is electrolysed in a solution containing about 2% of free nitric acid and 3% of silver in the form of nitrate. Silver, copper and some other metals are dissolved at the anodes, which are enclosed in bags, and silver is deposited at the cathodes which consist of rolled sheets of pure silver, slightly oiled to reduce adhesion. The current density is usually 20-30 amperes per sq. ft. of cathode. The silver may be deposited in a coherent form on the cathodes, with the help of a little gelatin in the electrolyte, and subsequently stripped off. Sometimes the cathodes are continually scrubbed with wooden brushes, working automatically, by which their surfaces are kept free from loose crystals of electro-deposited silver. The loose silver falls on to removable trays placed below. The gold remains undissolved at the anodes and retains some silver. The copper, lead, zinc, etc., accumulate in the electrolyte, which is kept in condition by the addition of acid and silver nitrate and by frequent renewal. The gold anodes are sometimes boiled in sulphuric acid, but if they contain as much as 950 parts of gold per 1,000, they may be melted at once and cast into anodes for treatment by the Wohlwill process. For observations on the conductivity of electrolytes used in the Mochius process, see Concord, Kern and Mulligan, *Trans. Amer. Inst. Min. Met. Eng.* 1926, **73**, 108. The Balbach-Thum process is similar to the Mochius process, the chief difference being that the electrodes are laid horizontally in trays, instead of being suspended vertically in bags in the electrolyte.

In the *Wohlwill process* (*Z. Electrochem.* 1898, **4**, 379, 402, 421; Rose and Newman, "Metallurgy of Gold," 7th ed., 1937, p. 481), the anodes contain not more than 50 parts of silver per 1,000 and a few parts per 1,000 of base metals. By the use of a "pulsating" current (a combination of a direct and an alternating current), gold with 15-17% silver can be refined, as the silver chloride is automatically detached from the anodes (Wohlwill, *Met. and Chem. Eng.*

1910, **8**, 82; Downs, *Metal Ind.* 1930, **36**, 141).

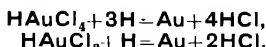
Under ordinary conditions with hot solutions at 60-70°, the electrolyte contains from 2.5 to 4% gold in the form of chloride and 3-5% HCl. At 20°, 10% HCl is used. With the pulsating current, less HCl can be used. The reactions at the anode are:



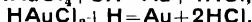
and



The hydrochloraurous acid subsequently decomposes in part into hydrochlorauric acid and metallic gold, which is found in minute particles in the anode mud. At the cathode the reactions are:



and



Some chlorine is evolved at the anode, especially if the temperature is too low, the hydrochloric acid insufficient in amount, or the current density too high, and some chlorine is taken up by silver and other impurities. The result is that the electrolyte gradually becomes weaker in gold chloride and more must be added at frequent intervals. The gold chloride for this purpose is usually prepared by dissolving gold in *aqua regia*. The  $\text{AuCl}_4^-$  ions migrate from the cathode and it is necessary to stir the solution by air-blowing or by a propeller. In pulsating-current practice, with an alternating current of strength 1.1 times that of the direct current, a direct current of 125 amperes per sq. ft. of anode can be used without scraping the anodes. In practice about 80 or 90 amperes per sq. ft. is usual. The amount of gold passing into the anode mud is diminished by the use of the pulsating current.

Platinum and palladium when alloyed with gold pass into solution from the anode and are subsequently recovered by chemical precipitation. Iridium, osmiridium and rhodium do not dissolve. Lead at the anode is converted into peroxide and causes passivity. It may also reach the cathode, making the gold brittle. It is accordingly removed beforehand together with selenium, tellurium, arsenic, antimony and bismuth by toughening. When the electrolyte becomes foul, owing to an accumulation of copper and other impurities, it is drawn off and the metals recovered. The electrolyte is renewed, most conveniently, by withdrawing a part of it each day and adding a solution of pure gold chloride. The anodes are made of such thickness (4-12 mm.) that they can be dissolved in 24 to 36 hours. The cathodes consist of fine gold and the deposited gold is usually from 999.5 to 999.9 fine. The residue at the anodes consists chiefly of silver chloride.

The process is particularly applicable to platiniferous gold, as in other refining processes platinum is left with the gold and lost.

*Chlorine Process.*—In Australia, South Africa and elsewhere, gold is refined by the passage of a stream of chlorine gas through the molten metal contained in a clay pot and covered with borax. The method was invented by Millor in 1867 (*J.C.S.* 1868, **21**, 506). The chlorine is at first completely absorbed and combines with all the

metals present except perhaps some of the platinum group. Gold itself is attacked very slightly in the earlier stages. The chlorides rise to the surface and are baled out, together with the borax, when they have become inconveniently bulky. Some chlorides volatilise and pass out of the furnace. In one modification, oxygen is added with the chlorine (Kahan, *Trans. Inst. Min. Met.* 1918, 28, 35). When the gold approaches a fineness of 990, gold chloride is formed in rapidly increasing amounts and begins to appear in appreciable quantities in the fumes which pass through the slag. The stream of chlorine, which has already been reduced to a mere trickle, is stopped soon afterwards. The end-point is marked by a peculiar stain (caused by gold chloride) on a cold clay pipe-stem held in the issuing fume. The remainder of the chloride slag is then removed and the gold cast into ingots. It is usually about 996 fine, the residue being mainly silver. Platinum remains with the gold. Tellurium is difficult to eliminate. If present, it remains to the end and is removed by additions of nitre.

The chloride slag is found to contain about 2% of the gold, mainly in the form of minute crystalline particles, reduced from chloride of gold which has passed into the slag (Law, 54th Ann. Rept. Royal Mint, 1923, p. 97). The gold is collected by the addition of carbonate of soda to the molten slag. Part of the silver chloride is reduced, and the metallic silver settles to the bottom, carrying the gold with it. This portion again passes through the process. The remainder of the silver is freed from the base chlorides and reduced with iron plates.

The process is especially suitable for refining bullion over 700 fine in gold, with the remainder mainly silver. Gold of lower fineness can be treated but the time of treatment becomes longer and the cost greater (*see* 64th Ann. Rept. Royal Mint, 1933, p. 110). If the silver is below 5%, there is some difficulty in removing base metals. The process is obviously unsuitable for doré bullion or platinumiferous gold. One great advantage is the rapidity of the process, as it brings 98% of the gold to account in a marketable form in a few hours. The plant costs little and the running costs are low.

**Properties of Gold.**—The characteristic yellow colour of gold is made redder by the presence of copper and paler by the presence of silver. In certain proportions the effect of one of the two metals neutralises that of the other. In a finely divided state, when prepared by volatilisation or precipitation, gold assumes various colours, such as deep violet, ruby and purple. "Faraday's gold" is a ruby coloured solution of colloidal metallic gold in water (Zugmondy, *Annalen*, 1898, 301, 29; J.C.S. 1912, 102, ii, 508). Molten gold is green.

Gold is the most extensible of all metals, and can be reduced by hammering to a thickness of 0.00008 mm. Its malleability and ductility are reduced by the presence of impurities, of which bismuth, lead and tellurium have the most striking effects. Gold containing 0.25 per 1,000 of bismuth is brittle. The melting-point of pure gold is 1063°, but if it contains 0.2% of tellurium, it softens at 432°, the melting-point

of the eutectic of gold and the compound  $\text{AuTe}_2$ . The presence of most other metals reduces the melting-point of gold, but it is raised by platinum. It begins to volatilise *in vacuo* in a quartz vessel at 1070° and boils at 800° under the same conditions (Krafft and Bergfeld, *Ber.* 1905, 38, 254). The density of cast gold is about 19.3, but that of precipitated gold is higher, and when gold is crystallised from solution its density is given as 19.43. It crystallises in the cubic system.

Gold is unaffected by the air at all temperatures and can be melted and solidified without being changed. In large pieces, it is not perceptibly attacked by alkalis or by nitric, sulphuric or hydrochloric acid, but, when finely divided, it is slightly soluble in boiling  $\text{HCl}$  and in boiling  $\text{HNO}_3$ . It is freely soluble in *aqua regia* or other mixtures, evolving one of the halogens, and more slowly in cyanide solutions in the presence of air. Its compounds are generally formed with difficulty and decomposed very easily with the liberation of the metal.

**Alloys of Gold.**—The gold-copper alloys are harder, more fusible, of higher tensile strength and less malleable and ductile than pure gold. The metals are miscible in all proportions when molten and on solidification separate only to a slight degree. The first additions of copper to gold cause a rapid lowering of the melting-point, the minimum of 884° being reached at the brittle alloy containing gold 82%, copper 18%. On cooling the solid solution of gold and copper which exists at high temperatures, gradual decomposition occurs with the formation of the compounds  $\text{AuCu}$  and  $\text{AuCu}_2$  (Haughton and Payne, *J. Inst. Metals*, 1931, 46, 457; Kurnakov and Ageew, *ibid.* 481; Grube, *Z. anorg. Chem.* 1931, 201, 41). The transition point is not far below 400°. The compound  $\text{AuCu}$  is hard and brittle and alloys containing much of it cannot be rolled or drawn. The effects are pronounced in the alloys containing 50–75% gold but are reduced by quenching (E. A. Smith, *Metal Ind.* 1932, 41, 28). The densities of the alloys when cast are as follows (Houtsema, *Z. anorg. Chem.* 1904, 41, 65):

Proportion of gold, %.	Density.
100	19.30
91.66	17.35
90.0	17.17
75.0	14.74
58.3	12.69
25.0	10.03

The densities of gold wares, which consist of triple alloys of gold, silver and copper, are higher.

**Gold-silver** alloys are soft, malleable and ductile and all their properties are intermediate between those of gold and silver. The colour is dominated by the silver, the alloy containing 37.5% of gold being only just distinguishable in colour from pure silver. Alloys containing not less than 65% of silver are almost completely parted by boiling nitric or sulphuric acid, the silver being dissolved and an allotropic form of gold left behind as a brown sponge or powder (Hanriot, *Bull. Soc. chim.* 1911, [iv], 9, 139, 339; *Compt. rend.* 1912, 155, 1085). The gold

obstinately retains about 0.1% of silver, and on continued boiling in strong nitric acid some gold is dissolved whilst the proportion of silver is reduced very slowly. The presence of copper facilitates the action of the acid but does not alter the final result.

**Amalgams** or alloys of gold and mercury are formed at ordinary temperatures by direct union of the two metals. Mercury dissolves 0.11% of gold at 0° and 0.126% at 100° (Kasantseff, Bull. Soc. chim. 1878, [ii], 30, 20), and gold absorbs mercury, forming a silver-white solid alloy containing about 40% of gold. At 440° most of the mercury is removed by volatilisation, the residue containing about 75% of gold. At a bright red heat, almost all the remainder of the mercury is distilled off. In the alternative, the mercury can be removed by dissolving it in nitric acid. Parravano (Gazzetta, 1918, 48, ii, 123) states that gold amalgams contain at least two compounds,  $\text{Au}_2\text{Hg}_3$  and  $\text{Au}_3\text{Hg}$  (cf. Paal and Steyer, Kolloid-Z. 1918, 23, 145); Plaksin (Am. Inst. Anal. Chim. Leningrad, 1928, 4, 336) gives the compounds as  $\text{AuHg}_2$  and  $\text{Au}_2\text{Hg}$ .

**Gold-iron** alloys are hard but malleable and ductile (Isaac and Tammann, Z. anorg. Chem. 1907, 53, 281; Nowack, Z. Metallk. 1930, 22, 97). Alloys containing between 15 and 20% of iron are used in jewellery in France under the name *or gris*. Their colour is greyish-yellow and they melt at temperatures higher than that of pure gold. *Or bleu* contains 25% of iron. It melts at a temperature of 1,160°.

Gold forms a brittle purple compound with aluminium,  $\text{AuAl}_2$  (aluminium 21.5%) (Heycock and Neville, Phil. Trans. 1900, A, 194, 201; 1914, A, 214, 267). The compound  $\text{AuZn}$ , containing 25% of zinc, is of a pale lilac colour and is also brittle. The compounds  $\text{Au}_3\text{Zn}$  and  $\text{AuZn}_2$  also exist (Soldau, J. Inst. Metals, 1923, 30, 351; 1926, 36, 454). Zinc removes gold from molten lead, and aluminium has the same property, the compound formed being  $\text{AuAl}_2$ .

**Uses of Gold.**—Gold is used in the form of its alloys with copper, silver, etc., in the manufacture of coin, plate and jewellery. Gold leaf is used for gilding by hand and potassium aurocyanide is used in gold plating baths. Gold is also used in photography (in the form of sodium chloraurate); in dentistry (as alloys); in medicine (as the chloride); and in the manufacture of mirrors for reflecting purposes. In the form of Purple of Cassius, and as leaf it is used for colouring and decorating glasses, glazes and enamels. Gold lace consists of extremely fine strips of gold twined round silk and contains about 2.5% of gold by weight. A large proportion of the gold production remains in the form of refined ingots which are used in international exchange.

**Gold Wares.**—The alloys used in the manufacture of gold wares consist of gold, silver and copper. The wares are usually made from rolled plates which are cut out by punches and struck between dies. The pieces are fitted together by hand, usually by means of soldering. Solders have fusion points lower than the gold objects with which they are to be used. They usually contain gold, silver, copper, zinc and

cadmium in proportions varying according to the colour of the alloy required. Decorative work is carried out by hand-hammering, engraving, chasing, etc. The wares are "coloured" or pickled by a process which removes the silver and copper from the surface and leaves a coating of pure gold, afterwards burnished. In pickling, the wares are heated to redness in air and the blackened surface is removed by boiling in dilute sulphuric or nitric acid, after which the colour is improved by immersion in hot mixtures of nitre, common salt, alum, etc. In the United Kingdom the 18-carat alloy (i.e.  $\frac{18}{24}$  gold) was introduced in 1477, the 22-carat alloy in 1573, and the 15-, 12- and 9-carat standards in 1854. In 1932 the 15- and 12-carat alloys were abolished as legal standards and in their place a new standard containing 585 gold per 1,000 was adopted, closely approximating to 14-carat gold (583.3 parts of gold per 1,000). The 9-carat alloys are used for the greatest amount of jewellery. They offer much scope for variations in colour. In addition to silver and copper the alloying metals include zinc, cadmium, nickel and occasionally iron. A small quantity of zinc is frequently added in the form of brass ("compo"). The zinc acts as a deoxidiser and assists in producing sound metal. The 14-carat alloys are also much used. Annealing at too high a temperature, say above 650°, or for too long a time impairs the working qualities of these alloys. Quenching at above 500° results in a greater degree of softness. Zinc is often added to both 14- and 18-carat alloys as a deoxidiser and degasifier (Carter, Amer. Inst. Min. Met. Eng., Tech. Publ. 86; E. A. Smith, Metal Ind. 1931, 39, 123; 1932, 41, 28).

Imitation gold wares sometimes consist of alloys of copper with aluminium, zinc, etc. "Rolled gold" (E. A. Smith, J. Inst. Metals, 1930, 44, 175) is made by sweating or soldering a sheet of gold alloy to a sheet of silver or base metal and then rolling. In "gold filled" wares, a gold sheet is soldered on each side of the base metal before the rolling. Electro-gilding is carried out in baths containing potassium aurocyanide with anodes of pure gold. Various colours of the deposit may be obtained according to temperature and current density (Sizelove, Monthly Rev. Amer. Electroplaters' Soc. 1931, 18, 45). Gilding by simple immersion in hot aurocyanide solutions is also practised. In mercurial gilding, gold amalgam is brushed over the surface of articles and the mercury driven off by heat.

**Gold Leaf** contains from 90 to 98% of gold, the rest being silver and copper. The metal is cast into little flat bars which are rolled out with frequent annealings until about 0.33 mm. thick. The strip of gold is then cut into pieces of 1 in. square and these are interleaved with vellum and beaten with a 16-lb. hammer to 4 in. square. They are again cut up and beaten out between gold-beaters' skins. The book of 25 leaves, each about  $3\frac{1}{2}$  in. (8.25 cm.) square, contains from 4 to 10 grains (0.26–0.65 g.) of gold. The leaves are from 0.00008 to 0.0002 mm. thick.

T. K. R.

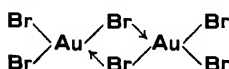
#### GOLD, THE COMPOUNDS OF.—

The chief classes of gold compounds are the aurous compounds in which the metal is uni-

valent and the auric compounds in which it is tervalent. There is an intermediate class, auroauric compounds, in the molecules of which there are equal numbers of univalent and tervalent gold atoms. Whenever gold is in aqueous solution either in the aurous or auric conditions it is always present as a complex ion and, as far as our present knowledge goes, there is no evidence for the existence in gold salts of the aurous ( $\text{Au}^+$ ) and of the auric ( $\text{Au}^{++}$ ) ion. In its compounds gold is always co-ordinated. In the typical aurous and auric compounds gold is 2-covalent and 4-covalent, respectively, and then has the corresponding effective atomic numbers of 82 and 84. In certain compounds which are exceptional aurous gold may be 4-covalent and auric gold may be 5-covalent; and in both cases gold then attains an effective atomic number of 86, corresponding to the atomic number of radon, the next inert gas (Dothie, Llewellyn, Wardlaw and Welch, J.C.S. 1939, 426; Brain and Gibson, *ibid.* 1939, 762). Recent investigations indicate that such compounds as auric bromide, auric chloride, aurous bromide, aurous chloride and aurous cyanide are not salts but are non-electrolytes. They are co-ordinated compounds in which the gold atom has a co-ordination number of four or two, depending on whether it is in the auric or aurous condition. This conception involves a revision of the constitution of many gold compounds. This may involve in some cases a change of nomenclature and, to emphasise the non-electrolytic character of the above simple compounds, they may be given the alternative names of tribromogold, trichlorogold, monobromogold, monochlorogold, moniodogold and monocyanogold respectively.

**Gold Tribromide** (auric bromide, tribromogold), is prepared by adding slowly at least twice the theoretical quantity of pure bromine to a weighed amount of pure and finely precipitated gold contained in a wide mouth glass flask provided with a ground stopper. The bromine and gold are brought into intimate contact and only sufficient cooling to avoid undue loss of bromine is employed during the mixing. When all the bromine has been added the contents are allowed to stand at the ordinary temperature for some hours in the stoppered flask. The flask with its stopper removed is then allowed to stand over sodium hydroxide until bromine vapour is no longer evident in the apparatus. The residue, a compact dark-red crystalline mass, is pure gold tribromide (Gibson and Colles, *ibid.* 1931, 2407).

Gold tribromide is decomposed by water, aurous bromide and hydrobromoaauric acid being produced. It is insoluble in ether, in the presence of which it undergoes decomposition, aurous bromide being formed and the ether becoming brominated. It is also insoluble in ether containing anhydrous hydrogen bromide and is sparingly soluble in bromine. Its molecular weight in boiling bromine indicates that its molecular formula is  $(\text{AuBr}_3)_2$  and its constitution is conveniently represented as:



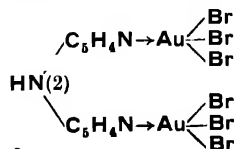
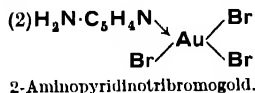
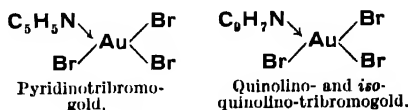
The magnetic susceptibility of gold tribromide at  $19^\circ$  is  $\kappa = -0.23 \times 10^{-6}$  c.m.u. On being heated in a closed evacuated tube, it undergoes dissociation below  $100^\circ$ ; the evolved bromine does not wholly recombine on cooling even after many months (Burawoy and Gibson, *ibid.* 1935, 217).

Gold tribromide is readily soluble in aqueous solutions of bromides and chlorides and such solutions afford the most convenient sources of hydrobromoaauric acid and its salts as well as of mixed chlorobromoaaurates.

**Hydrobromoaauric Acid,  $\text{HAuBr}_4 \cdot 3\text{H}_2\text{O}$**  (Lengfeld, Amer. Chem. J. 1901, 26, 324), may be conveniently obtained by the careful evaporation, finally under reduced pressure, over potassium hydroxide at the ordinary temperature, of a solution of gold tribromide in an aqueous solution of hydrobromic acid. It crystallises in long dark-red needles which are hygroscopic and soluble not only in water but also in ether. When carefully heated it becomes anhydrous and is then insoluble in ether.

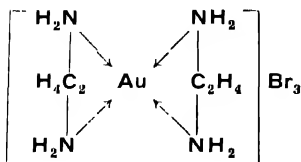
The salts of hydrobromoaauric acid with inorganic bases are best prepared by dissolving pure gold tribromide in an aqueous solution containing the calculated amount of the morganic bromide and evaporating the solution to crystallisation in a dust-free atmosphere. Although highly soluble, these deeply coloured salts, bromoaaurates, can be recrystallised from water. Many such salts are known and typical ones have the compositions:  $\text{NH}_4\text{AuBr}_4$ ;  $\text{NaAuBr}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{KAuBr}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{RbAuBr}_4$ ;  $\text{CsAuBr}_4$ ;  $\text{Mg}(\text{AuBr}_4)_2 \cdot 6\text{H}_2\text{O}$  (Gibson, private communication);  $\text{Ba}(\text{AuBr}_4)_2$ . A comprehensive series of bromoaaurates of organic bases has been described by Gutbier and Huber (Z. anorg. Chem. 1914, 85, 383). The X-ray examinations of the potassium salt have been carried out by Cox and Webster (J.C.S. 1930, 1635).

Co-ordination compounds of gold tribromide with suitable organic bases can be prepared either by the direct interaction of the gold compound and the base or by the following reaction:  $\text{MAuBr}_4 + \text{B} = \text{MBr} + \text{B} \cdot \text{AuBr}_3$  ( $\text{M} =$  univalent metal) (Gibson and Colles, *loc. cit.*). The following are the constitutional formulae of some of these non-electrolytic 4-covalent auric compounds:



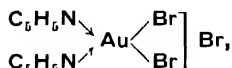
These co-ordination compounds are all deep red in colour and highly crystalline. They are stable and although sparingly soluble they can be recrystallised from solvents, *e.g.* chloroform and carbon tetrachloride which do not undergo oxidation or bromination.

When ethylenediamine is used in the above reaction the solution becomes pale yellow, and on addition of alcohol *diethylenediaminogold tribromide* (diethylenediaminoauric bromide)



crystallises in yellow glistening needles. This salt, in which auric and 4-covalent gold is part of a complex tervalent cation, like the co-ordination compounds described above, is decomposed by hydrobromic acid, hydrobromauric acid and the hydrobromide of the base being formed.

By recrystallisation of the compounds of the type,  $\text{B}\cdot\text{AuBr}_3$ , from the liquid base B, salts of the type  $(\text{B}_2\text{AuBr}_2)\text{Br}$  are formed. The compound *dipyridinodibromogold bromide*,



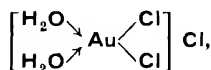
is a dark-red, crystalline, soluble salt which on being heated first loses a molecule of pyridine and is converted into the non-electrolyte, pyridinotribromogold, already mentioned.

*Diethylenediaminogold tribromide* (diethylenediaminoauric bromide) is analogous to the colourless crystalline salt *tetramminoauric nitrate*,  $[\text{Au}(\text{NH}_3)_4][\text{NO}_3]_3$  (Weitz, *Annalen*, 1915, 410, 117) which is prepared by adding a dilute solution of hydrochloroauric acid saturated with ammonium nitrate to a saturated solution of ammonia, treating the mixture with ammonia and washing the precipitate with water. It can be recrystallised from warm water. Examples of other salts which have been obtained are: the phosphate,  $\text{RPO}_4\cdot\text{H}_2\text{O}$ , the oxalonitrate,  $\text{RNO}_3(\text{C}_2\text{O}_4)$ , the perchlorate,  $\text{R}(\text{ClO}_4)_3$ , the oxaloperchlorate,  $\text{RClO}_4(\text{C}_2\text{O}_4)$ , the chlorate,  $\text{R}(\text{ClO}_3)_3$ , the sulphatonitrate,  $\text{R}(\text{NO}_3)(\text{SO}_4)$ , and the chromate,  $\text{R}_2(\text{CrO}_4)_3$  where  $\text{R}=[\text{Au}(\text{NH}_3)_4]^{+++}$ . All these salts are highly stable in the solid condition and retain their ammonia even in the presence of concentrated acids. The salts with halogen acids, hydrocyanic and thiocyanic acids have not been obtained.

Co-ordination compounds of gold tribromide with organic sulphides are also known. *Dibenzylsulphidotribromogold*,  $(\text{C}_6\text{H}_5)_2\text{S}\rightarrow\text{AuBr}_3$ , is prepared by the action of bromine on dibenzylsulphidomonobromogold (*see below*). It is a deep-red highly crystalline non-electrolyte, soluble in benzene, m.p. 129° (decomp.) (Gibson and Tyabji, private communication).

**Gold Trichloride** (auric chloride, trichlorogold) can be obtained by the direct action of a large excess of chlorine on finely divided pure gold (Rose, *J.C.S.* 1895, 67, 905). The reaction can be carried out even at 1,100°, although in the absence of excess of chlorine gold trichloride is completely decomposed at a lower temperature. The most convenient way of preparing the compound is by heating pure hydrochloroauric acid,  $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ , at 200° in a current of dry chlorine (Diemer, *J. Amer. Chem. Soc.* 1913, 35, 555).

Gold trichloride forms small, deep claret-red prismatic crystals (Pope, *J.C.S.* 1895, 67, 906). It is deliquescent and dissolves in water; from this solution by careful evaporation at the ordinary temperature orange-red crystals of the so-called dihydrate,  $\text{AuCl}_3\cdot 2\text{H}_2\text{O}$ , separate. This in all probability is a salt,



*diaquodichloroauric chloride*; it is not stable and tends to decompose, yielding aurous chloride (gold monochloride, monochlorogold) and hydrochloroauric acid.

The molecular weight of gold trichloride between 150° and 260° corresponds with the formula  $(\text{AuCl}_3)_2$  (W. Fischer, *Z. anorg. Chem.* 1929, 184, 333) and its constitution is analogous to that of gold tribromide (p. 111d).

The volatilisation and dissociation of the compound have been studied by a number of investigators, particularly Rose (*loc. cit.*) and Ephraim (Ber. 1919, 52, 241). At atmospheric pressure, gold trichloride dissociates into aurous chloride and chlorine at 254–256°, further decomposition of the aurous compound taking place at 290°.

The statement frequently made that gold trichloride (auric chloride) is soluble in alcohol, ether and other organic solvents is not correct. Willstätter (*ibid.* 1903, 36, 1803), who stated that gold chloride is soluble in ether, was investigating the properties of hydrochloroauric acid,  $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ , and this compound (*see below*) is soluble in ether. Many of the properties formerly ascribed to gold trichloride are those of hydrochloroauric acid and of sodium chloroaurate, and by "gold chloride" in certain recipes relating to the photographic process, etc., is frequently meant either hydrochloroauric acid or sodium chloroaurate. In the older literature "a solution of gold chloride" generally means "a solution of hydrochloroauric acid."

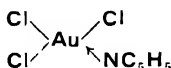
Gold trichloride is soluble in hydrochloric acid and *hydrochloroauric acid* is formed. When this solution is evaporated and finally left in a desiccator over potassium hydroxide the red crystalline residue has the composition



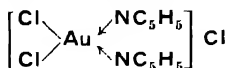
this compound is soluble in ether but the anhydrous acid is insoluble in that solvent. Theoretically, the chloroaurates may be obtained by neutralising a solution of hydrochloroauric acid with the appropriate base. In practice, the chloroaurate is more conveniently obtained when an excess of the appropriate cation is

present as provided by a solution of the chloride. The chloroaurates are also prepared by dissolving gold trichloride in a warm solution of the appropriate metallic chloride. A large number of chloroaurates have been described. The sodium and potassium salts,  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$  respectively, are both used for toning silver photographic prints (Kebler, J. Franklin Inst. 1900, **150**, 235; Johnston, J.S.C.I. 1901, **20**, 210). The ammonium salt has the composition  $\text{NH}_4\text{AuCl}_4 \cdot 3\text{H}_2\text{O}$ . The brown orthorhombic crystals obtained by Pollard (J.C.S. 1902, **117**, 99) by adding ammonium chloride to a solution of gold in *aqua regia* containing ammonium chloride, to which silver nitrate has also been added, are evidently those of a complex salt having the composition  $3\text{AgAuCl}_4 \cdot (\text{NH}_4)\text{AuCl}_4 \cdot 7\text{NH}_4\text{Cl}$ . The calcium, strontium and barium salts have the general formula  $\text{M}(\text{AuCl}_4)_3 \cdot 6\text{H}_2\text{O}$ . Numerous other inorganic salts have been described; they are generally characterised by being highly crystalline, soluble in water and of a deep yellow or orange colour. Chloroaurates of many organic bases have also been prepared, since these latter compounds have, in many cases, been identified through their salts with hydrochloroauric acid.

Co-ordination compounds of gold trichloride with organic bases are analogous to the corresponding compounds of gold tribromide and are prepared by similar methods. A convenient method of preparing the yellow *pyridinotrichlorogold*,



(cf. François, Compt. rend. 1903, **136**, 1557) is by dissolving sodium acetate in an aqueous solution of hydrochloroauric acid (not necessarily free from hydrochloric acid) and adding 1 mol. proportion of pyridine for each molecular proportion of hydrochloroauric acid. This non-electrolyte may be recrystallised from non-oxidisable solvents which do not undergo chlorination. When recrystallised from pyridine it is converted into the orange-coloured salt, *dipyridinodichloroauric chloride*,



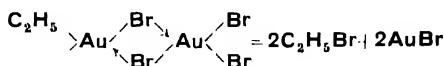
When this compound is gently heated it loses pyridine and is converted into pyridinotrichlorogold before undergoing more profound decomposition. Co-ordination compounds with dibenzyl sulphide and aliphatic sulphides having the general formula  $\text{R}_2\text{S} \rightarrow \text{AuCl}_3$  are well authenticated (Herrmann, Ber. 1905, **38**, 2813; Smith, J. Amer. Chem. Soc. 1922, **44**, 1769; Ray and Sen, J. Indian Chem. Soc. 1930, **7**, 67). The so-called salts of gold trichloride with sulphur tetrachloride, selenium tetrachloride and nitrosyl chloride are probably co-ordination compounds analogous to pyridinotrichlorogold. Gold trichloride also forms a complex compound with stannic chloride.

The evidence for the existence of the iodine derivative of tervalent gold is not conclusive.

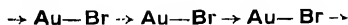
The early work on this substance as well as on the corresponding acid and salts, iodoaurates, needs repetition (cf. Johnston, Phil. Mag. 1836, [iii], **9**, 266).

There is also little satisfactory evidence for the existence of the fluorine derivative of tervalent gold.

**Gold Monobromide** (aurous bromide, monobromogold) produced by heating gold tribromide or hydrobromoauric acid is always likely to be contaminated with the metal. It can be obtained in a state of purity by heating monoethylbromogold (see p. 120d) at 50° to constant weight (about 30 minutes) the following reaction taking place:

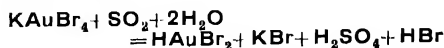


As the molecular weight of the compound has not been determined the molecular formula should for the time being be written  $(\text{AuBr})_n$  and the constitution is probably best represented thus:



When the compound is prepared by the above method (Burawoy and Gibson, J.C.S. 1934, 860; 1935, 218) it is obtained in yellowish-green crystals. It forms co-ordination compounds in which, as in the original compound, the aurous gold is 2-covalent. Examples of such co-ordination compounds are *pyridinomonobromogold*,  $\text{C}_5\text{H}_5\text{N} \rightarrow \text{Au}-\text{Br}$  (Burawoy and Gibson, l.c. 1935); the compound with phosphorus tribromide,  $\text{Br}_3\text{P} \rightarrow \text{Au}-\text{Br}$ ; *dibenzylsulphidomonobromogold*,  $(\text{C}_6\text{H}_5)_2\text{S} \rightarrow \text{Au}-\text{Br}$  (Gibson and Tyabji, 1937, private communication). The diammino compound is a salt having the constitution  $[\text{H}_3\text{N} \rightarrow \text{Au} \leftarrow \text{NH}_3]\text{Br}$  and described as *diamminoaurous bromide*.

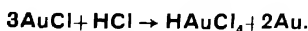
**Hydrobromoaurous Acid** has not been isolated but it is present in theoretical quantity in the solution obtained by reducing an ethylalcoholic solution of potassium bromoaurate by means of sulphur dioxide, the reaction taking place being:



The colourless solution is stable and if excess sulphur dioxide has been used it may be expelled by heating the solution on the water bath. It can be filtered from precipitated potassium bromide, and on long exposure to air, or considerable dilution with water, gold is precipitated and the solution becomes coloured owing to the formation of bromoaurate (Brain, Gibson and Imperial Chemical Industries Limited, B.P. 497746).

**Gold Monochloride** (aurous chloride, monochlorogold) has probably a constitution analogous to that of the corresponding bromine compound. It is a yellowish powder formed by heating the trichloride at 170–180°; at higher temperatures further decomposition takes place (Rose, J.C.S. 1895, **67**, 881, 905; Campbell, Trans. Faraday Soc. 1907, **3**, 103). It is insoluble in water and

is slowly attacked by hydrochloric acid, gold and hydrochloroauric acid being produced,

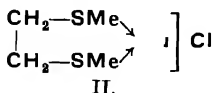
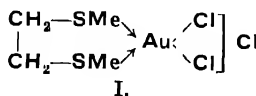


When an alcoholic solution of a chloroaurate is reduced with sulphur dioxide the solution becomes paler in colour but does not become colourless and gold separates after some time in quantitative amount. If hydrochloroaurous acid is formed it is evidently less stable than hydrobromoaurous acid (*see above*). Certain salts of hydrochloroaurous acid which have been described do not appear to have been definitely authenticated.

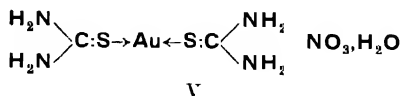
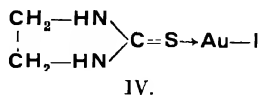
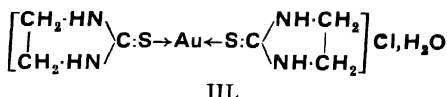
A number of co-ordination compounds of gold monochloride have been described; examples of these are the compound with phosphorus trichloride,  $\text{Cl}_3\text{P} \rightarrow \text{Au}-\text{Cl}$ , and compounds of the general formula  $\text{R}_3\text{P} \rightarrow \text{Au}-\text{Cl}$  and  $\text{R}_3\text{As} \rightarrow \text{Au}-\text{Cl}$  (Mann, Wells and Purdie, J.C.S. 1937, 1828) where R=alkylgroup. These alkylphosphine and alkylarsine derivatives are volatile and the former yield brilliant gold films when their vapours are heated. *Ammunomonochlorogold* and *dibenzylsulphidomonochlorogold*,  $(\text{C}_6\text{H}_5)_2\text{S} \rightarrow \text{Au}-\text{Cl}$  (Herrmann, Ber. 1905, 38, 2813) are compounds of similar type.

**Diamminoaurous Chloride** (Ephraim, *ibid.* 1919, 52 [B], 241) is analogous to the corresponding bromine compound and is a salt having the constitution  $[\text{NH}_3 \rightarrow \text{Au} \leftarrow \text{NH}_3]\text{Cl}$ . In all these co-ordination compounds the aurous gold atom is 2-covalent. Compounds containing 3 and 12 mol. of ammonia to each molecule of gold monochloride have been described (*see below*).

Sulphur compounds structurally analogous to diamminoaurous chloride have been investigated by Morgan *et al.* (J.C.S. 1922, 121, 2882; 1928, 143). By adding dimethyldithioethylene,  $\text{CH}_3\text{S}-\text{C}_2\text{H}_4-\text{SCH}_3$ , to hydrochloroauric acid dissolved in ether the yellow *dichloro-dimethylthioethyleneauric chloride* (I) is precipitated and in the presence of moisture this is converted into *dimethyldithioethyleneaurous chloride* (II).



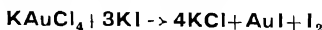
By interaction of hydrochloroauric acid and ethylenethiocarbamide *bisdiethylenethiocarbamidoaurous chloride* (III) is obtained in colourless crystals. The corresponding nitrate (anhydrous) and bromide ( $1\text{H}_2\text{O}$ ) and oxide are also described together with the non-electrolyte *ethylenethiocarbamidoiodogold* (IV). From thiocarbamide, Morgan and Ledbury obtained the colourless crystalline *bisthiocarbamidoaurous nitrate* (V) as well as the anhydrous compound (*cf.* Reynolds, J.C.S. 1869, 1).



The constitutions of the non-electrolytes  $(\text{NH}_3)_3\text{AuCl}$  (Meyer, Compt. rend. 1906, 143, 280),  $(\text{NH}_3)_2\text{P}(\text{OMe})_3\text{AuCl}$  (Levi-Malvano, Atti. R. Acad. Lincei, 1908, 17, 857) do not necessarily conflict with the stable 2-covalency of the aurous gold atom and such compounds may contain co-ordinated hydrogen atoms. On the other hand, certain investigators (*cf.* Mann, Wells and Purdie, *l.c.*) regard such compounds as containing 4-covalent aurous gold (*see below*). The substance stated to have the composition  $\text{AuCl} \cdot 12\text{NH}_3$  (Meyer, Compt. rend. 1901, 133, 815) and prepared by the action of ammonia on gold monochloride at  $-28^\circ$  easily loses ammonia and is converted into the stable diamminoaurous chloride mentioned above.

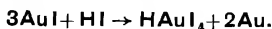
Fluorine has no action on gold at the ordinary temperature but is stated to corrode the metal at higher temperatures. It is doubtful whether a compound having the empirical formula  $\text{AuF}_3$  has been isolated and no corresponding aurous compound has been described.

**Gold Monoiodide** (aurous iodide, moniodogold) having the empirical formula  $\text{AuI}$  is prepared by the action in aqueous solution of potassium iodide on potassium chloroaurate,



The precipitated compound is freed from admixed iodine by gently warming ( $35^\circ$ ); unless special precautions are taken metallic gold is generally present. If excess of potassium iodide is used some gold remains in solution indicating the possibility of the formation of a salt,  $\text{KAuI}_2$  or  $\text{KAuI}_4$ ; but such compounds have not been isolated.

Aurous iodide is a yellow crystalline powder which is decomposed by hydriodic acid and by an aqueous solution of potassium iodide, metallic gold being produced. It has been suggested that hydroiodoauric acid (or the potassium salt) may be present in the solution

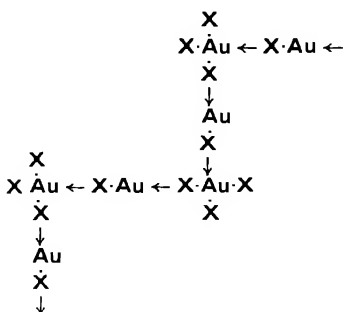


Like other aurous halides aurous iodide forms compounds with ammonia of which the most stable is *ammunomonoiogold*,  $\text{H}_3\text{N} \rightarrow \text{Au}-\text{I}$  (Meyer, *l.c.*). *Triethylphosphinomonoiogold*,  $(\text{C}_2\text{H}_5)_3\text{P} \rightarrow \text{Au}-\text{I}$ , m.p.  $40^\circ$ , *tri-n-butylphosphinomonoiogold*,  $(\text{C}_4\text{H}_9)_3\text{P} \rightarrow \text{Au}-\text{I}$ , b.p.  $220-225^\circ/0.2 \text{ mm.}$ , and *trimethylarsinomonoiogold*,  $(\text{CH}_3)_3\text{As} \rightarrow \text{Au}-\text{I}$ , m.p.  $176-178^\circ$  (Mann,



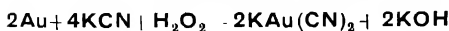
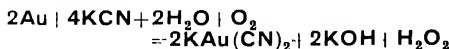
Wells and Purdie, *l.c.*) are stable compounds and afford further examples of the 2-covalency of aurous gold.

There is some doubt concerning the existence of the so-called auroauric bromide and chloride, compounds having the general empirical formula  $\text{AuX}_3$ . Neither of these compounds has been adequately described, but there is reason for believing that they may be capable of existing under certain conditions and if so it is suggested that their constitutions may be represented thus:



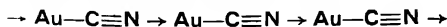
*i.e.* as a zig-zag chain containing alternate tervalent and 4-covalent auric gold atoms and univalent and 2-covalent aurous gold atoms. A formerly suggested constitution,  $\text{Au}[\text{AuX}_4]$ , representing the compounds as aurous salts is much less probable.

**Cyanides.**—In the presence of air or oxygen gold dissolves in an aqueous solution of potassium (sodium) cyanide, the following reactions taking place:



This is the basis of the McArthur-Forrest process (1887) most extensively used in gold extraction (*q.v.*). The gold goes into solution as the potassium (sodium) *aurocyanide* which can be obtained in colourless crystals by careful evaporation of a solution of gold monocyanide (aurous cyanide, monocyanogold, *see below*) containing the calculated quantity of potassium (sodium) cyanide.

**Gold Monocyanide** (aurous cyanide, monocyanogold) was originally prepared by adding hydrochloric acid to an aqueous solution of potassium aurocyanide, carefully evaporating the solution to dryness and washing the product with water. It is obtained pure as a somewhat yellowish powder by gently heating the dialkylmonocyanogold compounds (*see below*) above their melting-points. Its molecular weight has not yet been determined and the molecular formula should be written as  $(\text{AuCN})_n$ , its constitution being represented thus,



(Gibson, *Proc. Roy. Soc.* 1939, A, 173, 160; *cf.* West, Z. Krist. 1935, 90, 555).

**Potassium Aurocyanide**,  $\text{KAu}(\text{CN})_2$  (*see above*), is obtained by crystallisation of the aurous

solution prepared by dissolving gold in the presence of air or oxygen in an aqueous solution of potassium cyanide or by crystallising a solution of aurous cyanide in aqueous potassium cyanide solution. It is present in the aqueous solution obtained by the addition of potassium cyanide to hydrochloroauric acid. It is a colourless crystalline salt which yields colourless solutions in water (solubility, 14.3 g. in 100 c.c. at the ordinary temperature and 200 g. in 100 c.c. at 100°). According to Rose and Newman ("The Metallurgy of Gold," 1937, p. 73), the aqueous solution of potassium aurocyanide used for the electro-deposition of gold may be prepared (i) by dissolving the "fulminating gold," precipitated by adding ammonia to hydrochloroauric acid, in potassium cyanide, or (ii) by dissolving purified auric hydroxide (*see below*) in aqueous potassium cyanide, or (iii) by passing an electric current through an aqueous solution of potassium cyanide using a gold anode.

The precipitation of gold from aqueous solutions of potassium (sodium) aurocyanide which can be represented in its simplest form by the equation



is used industrially. Other metals more electropositive than gold may be used. Oxalic acid, sulphurous acid and mercurous chloride are stated to precipitate aurous cyanide from aqueous solutions of potassium aurocyanide.

Aurocyanides of sodium, ammonium, calcium, barium, zinc and cadmium have been prepared. Like potassium aurocyanide, all these yield a precipitate of aurous cyanide with evolution of hydrogen cyanide when treated with mineral acids. Co-ordination compounds of potassium aurocyanide with 2:2'-dipyridyl and 4:5-(*o*-)phenanthroline in which the aurous gold atoms are 4-covalent have been investigated by Dohue, Lowellyn, Wardlaw and Welch (*J.C.S.* 1939, 426).

The cyano derivative of tervalent gold (auric cyanide) has not been prepared.

**Potassium Auricyanide** (potassium cyanaurate),  $2\text{KAu}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ , is described as being obtained in colourless crystals by adding an aqueous solution of potassium cyanide to sodium chloroaurate until the precipitate formed redissolves, and carefully evaporating the solution which should be colourless (*see* Potassium Aurocyanide). Derivatives of potassium auricyanide (cyanaurate) in which the cyanogen radical is replaced by halogens (not fluorine) have been described (Lindbom, *Ber.* 1877, 10, 1725).

**Oxides of Gold.**—The lower oxide of gold, which would be expected to have the empirical formula  $\text{Au}_2\text{O}$ , does not exist. A critical and experimental review of the composition of the material prepared as described by Figuier (*Ann. Chim. Phys.* 1844, [iii], 11, 339), by Kruss (*Annalen*, 1887, 237, 276) and by his own more suitable methods has been made by Pollard (*J.C.S.* 1926, 1347), who concludes that material described as "aurous oxide" is a mixture of gold and auric oxide ( $\text{Au}_2\text{O}_3$ ) and does not exhibit reactions of aurous compounds.

**Gold Trihydroxide** (auric hydroxide) having

the empirical formula  $\text{Au}(\text{OH})_3$  is obtained (i) by heating an aqueous solution of hydrochloroauric acid with excess of magnesium oxide and washing the precipitate thoroughly with dilute nitric acid, (ii) by adding an aqueous solution of potassium hydroxide to one of hydrochloroauric acid until the precipitate just redissolves, boiling the dark brown solution until the supernatant liquid becomes pale yellow, adding a slight excess of sulphuric acid and washing the precipitate. It may be further purified by dissolving the precipitate in concentrated nitric acid, precipitating finally with water and drying under reduced pressure.

When allowed to stand over phosphorus pentoxide it is converted into a substance which has been described as *auryl hydroxide* but which may be the unstable *auric acid*,  $\text{H}[\text{AuO}_2]$ . When the trihydroxide is heated at  $140^\circ$  it is converted into auric oxide,  $\text{Au}_2\text{O}_3$ , a brown powder (Kruss, *Annalen*, 1887, 237, 290).

When auric hydroxide is warmed with alcoholic potassium hydroxide it is reduced to the metal, which is frequently deposited in small glistening scales used in mediæval times in painting miniatures. By the action of hydrochloric and hydrobromic acids, auric hydroxide is converted into hydrochloroauric and hydrobromoauric acids respectively.

Auric hydroxide is soluble in an aqueous solution of potassium hydroxide and this solution on evaporation at the ordinary temperature under reduced pressure yields small pale-yellow needles of *potassium aurate*,  $\text{KAuO}_2 \cdot 3\text{H}_2\text{O}$ . Aqueous solutions of this salt are strongly alkaline. The corresponding barium salt,  $\text{Ba}(\text{AuO}_2)_2 \cdot 5\text{H}_2\text{O}$ , is sparingly soluble in water. Other salts are also known.

The so-called *auroauric oxide* having the empirical formula  $\text{AuO}$ , and which would correspond to halogen compounds having the general empirical formula  $\text{AuX}_2$  (see above), is described as being produced by heating auric hydroxide at  $160^\circ$  (Kruss, *Ber.* 1886, 19, 2541).

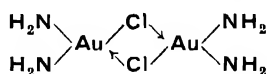
**Sulphides.**—It would appear that the early work (Ditte, *Compt. rend.* 1895, 120, 320; Levöl, *Ann. Chim. Phys.* 1850, [iii], 30, 355; Hoffmann and Kruss, *Ber.* 1887, 20, 2674) on the compounds of gold and sulphur having the empirical formulae  $\text{Au}_2\text{S}$  and  $\text{AuS}$ , respectively, and produced by the action of hydrogen sulphide on solutions of aurocyanides and chloroaurates, respectively, needs revision. The salt, *sodium aurosulphide*,  $\text{NaAuS}_4 \cdot 4\text{H}_2\text{O}$ , corresponding to a sulphide,  $\text{Au}_2\text{S}$ , is obtained by heating metallic gold with sodium sulphide and sulphur, extracting the fused mass with water, filtering and evaporating the solution in an inert atmosphere at the ordinary temperature. The salt crystallises in colourless monoclinic prisms which rapidly become brown on exposure to air. The solution of gold in "liver of sulphur" was known to Glauber and Stahl.

**Auric Sulphide**,  $\text{Au}_2\text{S}_3$ , was described as being obtained as a deep yellow precipitate by treating anhydrous lithium chloroaurate with hydrogen sulphide at  $-10^\circ$  (Antony and Lucchesi, *Gazzetta*, 1890, 20, 601; 1891, 21, ii, 209), but this method of preparation seems unlikely to lead to a pure product. Gutbier

and Dürrwächter (*Z. anorg. Chem.* 1922, 121, 266), who could not prepare the other sulphides (see above), obtained the pure auric sulphide by passing a rapid stream of hydrogen sulphide at  $-2^\circ$  through a dilute (less than 2%) solution of hydrochloroauric acid in *N*-hydrochloric acid. It is a dark-coloured powder soluble in sodium sulphide forming sodium aursulphide having probably the formula  $\text{NaAuS}_2$  analogous to  $\text{NaAuCl}_4$ . It is also soluble in potassium sulphide solution.

**Fulminating Gold.**—There are several varieties of the explosive substances known by the historic name of "fulminating gold." Earlier work on this difficult subject (Dumas, *Ann. Chim. Phys.* 1830, [ii], 44, 167; Raschig, *Annalen*, 1886, 235, 341) has been the subject of a critical review and a detailed experimental study by Weitz (*ibid.* 1915, 410, 117–222).

Some of the better known "fulminating golds" (if individual substances) contain halogen in addition to nitrogen, which must always be present. The greyish precipitate obtained by the action of excess of ammonia on an aqueous solution of hydrochloroauric acid appears to be a mixture (*A*) of two compounds to which the formulae  $\text{Au}_2\text{O}_3 \cdot 3\text{NH}_3$  (*sesqui-amminoauric oxide*) and  $\text{HN}:\text{AuCl} \cdot \text{NH}_2$  (*amino-iminoauric chloride*) have been assigned. Assuming the correctness of such formulae for explosive substances, it is not surprising that they do not necessarily conform to the formulae of normal gold compounds. The yellow precipitate obtained by adding a dilute solution of hydrochloroauric acid containing ammonium chloride to a cold saturated solution of ammonium chloride containing ammonia is stated to be an individual and to have the formula  $\text{Au}(\text{NH}_2)_2\text{Cl}$  (diammoauric chloride) and is not explosive. This compound is stated to contain water, but the compound itself may be a normal auric compound having the constitution :



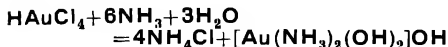
Treatment of this compound with an excess of water furnishes an explosive compound containing no halogen and to which the empirical formula  $3\text{AuO} \cdot 2\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  has been assigned, and such a formula does not appear to be that of a normal gold compound.

One of the most sensitive of the "fulminating golds" has been given the formula  $\text{Au}_2\text{O}_3 \cdot 2\text{NH}_3$ . It is a black substance the constitution of which cannot be formulated as that of a normal auric compound. It is obtained by treatment with hot water of *sesqui-amminoauric hydroxide*,  $2\text{Au}(\text{OH})_3 \cdot 3\text{NH}_3$ , which is itself obtained by the action of excess of ammonia on the mixture (*A*) mentioned above.

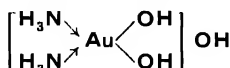
In the light of our present information, the proposed classification of "fulminating golds" into two types of compounds in which the atomic ratios of gold to nitrogen are respectively 1:1 and 2:3 cannot be adhered to rigidly. It is probable that more satisfactory knowledge regarding the constitution of "fulminating golds" may be obtained, as indicated by Weitz

(*l.c.*), by a further study of tetramminoauric compounds some of which have been referred to above. Alkaline aqueous solutions of tetramminoauric nitrate on standing yield explosive precipitates.

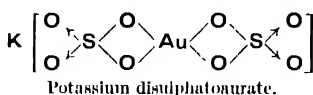
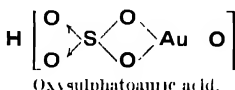
One variety of "fulminating gold" has been prepared by a reaction which may be represented thus:



It is a yellow precipitate, explosive but not so sensitive as other varieties mentioned above. The compound may be diamminodihydroxyauric hydroxide having the constitution:



**Salts.**—Since gold does not yield salts containing either aurous or auric ions the existence of such compounds as the so-called aurous sulphate, auric sulphate and auric chromate is very doubtful. On the other hand, Schottländer (*ibid.* 1883, 217, 312) by the action of concentrated sulphuric acid on "auryl nitrate" (*see below*) at 200° obtained yellow octahedra of what he described as *auryl hydrosulphate*,  $\text{AuO} \cdot \text{HSO}_4$ . When this compound is treated with one-tenth of its weight of potassium hydrogen sulphate and the mixture evaporated at 200° it yields yellow rhombic crystals of what he described as *potassium disulphatoaurate*. It also prepared the corresponding silver salt. The constitution and systematic name of each of these substances may be respectively,



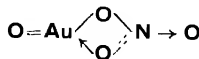
For similar reasons, the existence of compounds which have been described as aurous and auric nitrates must be regarded as doubtful. Again, on the other hand, Schottländer (*l.c.*) obtained golden-yellow triclinic crystals of *hydronitratouric acid* by cooling the solution of auric hydroxide in nitric acid (density, 1.5) in a freezing mixture. The same acid was obtained by Jeffery (Trans. Faraday Soc. 1916, 11, 172) by electrolysis nitric acid (1:2) using a porous pot and a gold anode and evaporating the yellowish-brown anodic solution over sulphuric acid and sodium hydroxide. The acid is decomposed by water and both authors assign to it the formula  $\text{H}[\text{Au}(\text{NO}_3)_4] \cdot 3\text{H}_2\text{O}$ , analogous to hydrochlorauric and hydrobromauric acids,  $\text{H}[\text{AuX}_4] \cdot 3\text{H}_2\text{O}$ . The ammonium, potassium and rubidium salts have been described by Schottländer.

The *auryl nitrate* which Schottländer (*l.c.*) obtained as an amorphous mass by dissolving

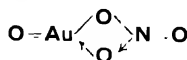
auric hydroxide in nitric acid (density, 1.4 and to which he gave the formula



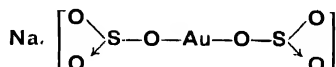
may not be a salt in the strict sense of the term; in accordance with the 4-covalency of tervalent gold its constitution may be written as



or, less likely, as



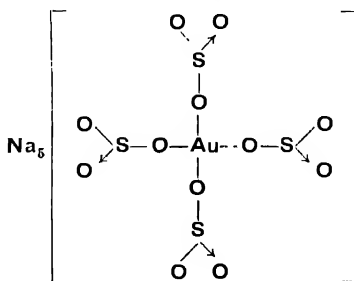
A number of complex sulphites have been described. One of these (Himly, Annalen, 1846, 59, 95) having the formula  $\text{Na}_5\text{Au}(\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$  may be an aurous compound having the constitution:



The yellow compound having the formula



(Oddo and Mingoia, Gazzetta, 1927, 57, 820; cf. Rosenheim, Hertzmann and Pritze, Z. anorg. Chem. 1908, 59, 198) and which is prepared by neutralising hydrochlorauric acid with sodium hydroxide and adding a solution of sodium sulphite, filtering and precipitating with alcohol may, bearing in mind its colour, be an auric compound having the constitution:



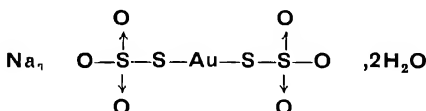
The corresponding potassium salt has also been prepared.

**Sodium Aurothiosulphate**, Fordos and Gélus' salt (Ann. Chim. Phys., 1845, [iii], 13, 344), although long known as a complex aurous compound and used in the toning of silver photographic prints, has been of considerable interest since 1924 when it was introduced by Møllgaard of Copenhagen under the name "*Sanocrysin*" for the treatment of tuberculosis. Later, along with many other complex aurous compounds, it has been used in the treatment of rheumatoid arthritis, and it is not improbable that "gold therapy" may be extended considerably (*see below*). Its constitution has been expressed by

the formula  $3\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Au}_2\text{S}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  which cannot be correct since this colourless crystalline salt gives no reactions of a thiosulphate and aurous gold does not form salts containing aurous ions.

It was originally prepared by the gradual addition of a 2% solution of sodium chloroaurate to an aqueous solution containing 4 mol. proportions of sodium thiosulphate. After the red liquid had become colourless the salt was precipitated by the addition of alcohol and was purified either by repeated precipitation from its aqueous solution by means of alcohol or by recrystallisation from water. In the preparation just described part of the sodium thiosulphate reduces the auric compound to the aurous condition, being itself converted into tetrathionate. Consequently several modifications of the preparation have been introduced. These consist essentially in carrying out the reaction using suitable reducing agents whereby all the sodium thiosulphate employed reacts with the reduced gold compound as soon as it is formed.

The constitution of the compound should be expressed thus:

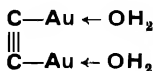


in keeping with the 2-covalency of aurous gold and with the fact that the compound does not give the usual thiosulphate reactions. The corresponding barium salt has been prepared by double decomposition between the sodium salt and barium chloride and the free acid has been obtained by treating the barium salt with the calculated quantity of sulphuric acid.

Sodium aurothiosulphate is somewhat sparingly soluble in water at the ordinary temperature and possesses a curiously sweet taste. It is stable but, as ordinarily prepared, when exposed to air it becomes yellowish-brown, decomposition having set in. Its solution is not reduced by ferrous sulphate or oxalic acid nor decomposed by hydrochloric acid. When acetylene is passed into its aqueous solution the so-called *aurous acetylides*,  $\text{C}_2\text{Au}_2$ , is produced as a yellow precipitate which is explosive when dry (Matthews and Watters, J. Amer. Chem. Soc. 1900, 22, 108; v. Vol. II, 280b, 281b). The constitutional formula



is not in keeping with the 2-covalency of aurous gold, which would however be satisfied by the formula



Like other acetylides, it is decomposed by hydrochloric acid yielding acetylene and, in this case, gold monochloride.

**Complex Imido Compounds.**—A number of complex succinimido derivatives mostly containing auric gold have been described by Pope (B.P. 338506/1929; B, 1931, 319). The compounds are prepared from auric hydroxide, chloroaurates, hydrochloroauric acid or fuming gold and succinimide in the presence of ammonia or amines. Among the compounds isolated are:

$[(\text{NH}_3)_2\text{AuSn}_2]\text{Cl}$ , diamminodisuccinimidoauric chloride,

$[(\text{NH}_3)_2\text{AuSn}_2][\text{AuCl}_4]$ , diamminodisuccinimidoauric chloroaurate,

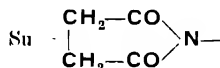
$[(\text{NH}_2\text{Me})_2\text{AuSn}_2]\text{Cl}$ , dimonomethylamminodisuccinimidoauric chloride,

$[(\text{NHEt}_2)_2\text{AuSn}_2]\text{Cl}$ , didiethylamminodisuccinimidoauric chloride,

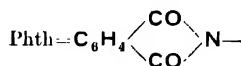
$[(\text{NHEt}_2)_2\text{AuSn}_2]\text{AuSn}_2$ , didiethylamminodisuccinimidoauric succinimidoaurate,

$\text{NH}_3\text{AuSn}_3$ , monoamminotrisuccinimidogold,

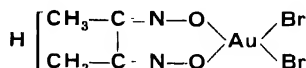
together with salts of hydrosuccinimidoaurous acid,  $\text{H}[\text{AuSn}_2]$ , and salts of dichlorodisuccinimidoauric acid,  $\text{H}[\text{Cl}_2\text{AuSn}_2]$ , where



Other examples of complex imido compounds belonging to this series are hydrodiphthalimido-hydroxyauric acid,  $\text{H}[\text{Phth}_2\text{Au}(\text{OH})_2]$ , where



(Gibson and Tyabji, private communication) and hydrodimethylglyoximylbromoauric acid,

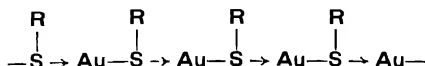


(Brain and Gibson, private communication). Complex derivatives (imidoauric acids) of succinimide, phthalimide, 5:5-diethylbarbituric acid and *o*-benzoisulphinide (saccharin) have also been described by Kharasch and Isbell (J. Amer. Chem. Soc. 1931, 53, 3059).

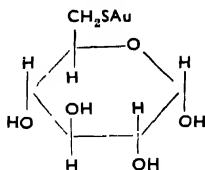
**Other Inorganic Gold Compounds Containing Complex Organic Radicals.**—In view of the use of complex (chiefly aurous) compounds in the therapeutic treatment of tuberculosis (see Sodium Aurothiosulphate, "*Sanocrysin* ") and their increasing application in the treatment of other conditions, especially rheumatoid arthritis, a large and rapidly increasing number of aurous derivatives of organic compounds have been prepared, generally by methods which are the subjects of patents (cf. "Handbuch der Chemotherapie," Fischl and Schlossberger, Fischers Medizinische Buchhandlung, Leipzig, 1934). The compounds are generally prepared by the action of the organic compound (part of which acts as a reducing agent) on alkali halogenoaurates (usually sodium chloroaurate) or by their interaction in the presence of a suitable reducing agent (sodium sulphite, etc.).

Many of the compounds are soluble in water and such aqueous solutions may be administered intravenously; others may not be soluble in water and these as well as the former may be administered intramuscularly in oil suspension.

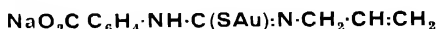
Many of the aurous compounds which have been described are derivatives of substances (such as mercaptans) containing the  $-SH$  group and in the literature are frequently given the constitutional formula of the general type  $-SAu$ . Such a general formula does not allow for the 2-covalency of aurous gold and cannot be correct. The simplest aurous derivatives of mercaptans are generally highly insoluble compounds having high molecular weights. Their constitution may be written  $(R-S-Au)_n$  or, in extended form, as



The following are four typical aurous derivatives of organic compounds which (in addition to sodium aurothiosulphate, frequently known as "*Sanocrysin*," but other proprietary names have also been allotted to it) have found considerable therapeutic application: "*Solganol B*" described as goldthioglucoase and, in the literature, given the constitutional formula



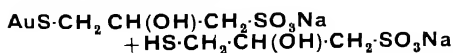
"*Lopron*" is sodium 3-allylgoldthionrebenzoate and in the literature is given the formula (G.P. 551421)



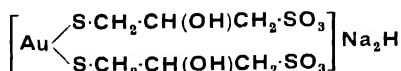
"*Myochrysin*" is disodium aurothiomalate and stated to have the formula



"*Allochrysin*" (Lumière and Perrin, *Compt. rend.* 1927, **184**, 289) is given in the literature the constitutional formula



but this compound may have a constitution analogous to that of sodium aurothiosulphate thus:



#### ORGANIC COMPOUNDS OF GOLD.

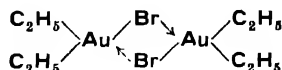
Apart from the already known cyano compounds and the acetylides (*see above*), the first typical organic compounds of gold were prepared by Pope and Gibson (*J.C.S.* 1907, **91**, 2061);

and their investigation has been carried out chiefly by Gibson *et al.* (*ibid.* 1930, 2531; 1931, 2407; 1934, 860; 1935, 219, 1024; 1937, 1690; 1939, 762; *Ann. Report Brit. Assoc.* 1938, 35).

*Diethylmonobromogold*,  $(Et_2AuBr)_2$ , may be prepared starting from hydrobromauric acid,  $HAuBr_4 \cdot 3H_2O$ , gold tribromide,  $(AuBr_3)_2$ , pyridinotribromogold,  $C_5H_5NAuBr_3$ , or, most conveniently, from the corresponding trichlorogold compound.

To a mechanically stirred suspension of pyridinotrichlorogold (10 g.) in dry pyridine (200 c.c.) at 0° is added a filtered solution of ethylmagnesium bromide (2.2 mol.) in ether (45 c.c.). Water (100 c.c.) at 0° is then added followed by ligroin (b.p. 60–80°; 300 c.c.) and then hydrobromic acid (*d* 1.49; 300 c.c.) at such a rate that the temperature does not rise above 40°. The liquid (two layers) is filtered from solid matter and the ligroin solution separated. The aqueous solution is extracted several times with ligroin. To the combined ligroin extracts, after washing with water, ethylenediamine is added until no further colourless precipitate (ethylenediaminediethylgold bromide, *see below*) is produced. The colourless precipitate is dissolved by shaking the ligroin suspension with water and the separated aqueous solution acidified with hydrobromic acid. The colourless precipitate, diethylmonobromogold, is separated, washed with water and dried at the ordinary temperature. It may be purified by dissolving in redistilled ligroin (b.p. 40–60°) and allowing the solution to evaporate at the ordinary temperature.

Diethylmonobromogold crystallises from ligroin in soft colourless anorthic needles, m.p. 58° (decomp.). It is soluble in all the usual organic solvents and when pure is fairly stable, decomposing superficially (violet colour) on exposure to light. Its molecular weight in freezing benzene and bromoform shows that the molecular formula is  $(Et_2AuBr)_2$  and its constitution may be conveniently expressed as



the auric gold atoms being 4-covalent. This constitution is in agreement with the results of X-ray crystallographic investigation which has also shown that the four valencies attached to the 4-covalent auric atoms are planar. Diethylmonobromogold and certain related organic gold compounds when dissolved in a suitable solvent (*e.g.* ethanol) undergo an interesting spontaneous decomposition at the ordinary temperature on treatment with alkali or alkali metal alcoholate; brilliant gold films are produced which can be deposited on a variety of surfaces (Gibson, B.P. 497240).

The following derivatives among others have been prepared:

*Ethylenediaminediethylgold bromide*,

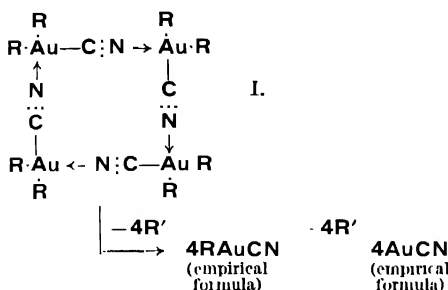


a stable colourless crystalline salt, decomp. from 182°, soluble in water (*see above*).



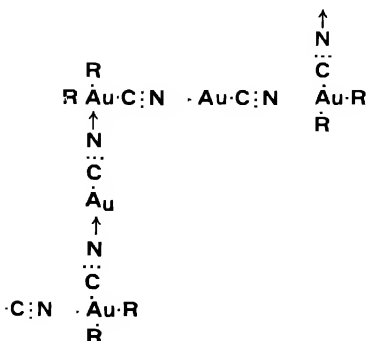
formula  $(R_2AuCN)_4$  and their constitution is represented by (I). This has been completely confirmed by the results of dipole moment determinations and by X-ray crystallographic investigations (Phillips and Powell, Proc. Roy. Soc. 1939, A, 173, 147).

*Diethylmonocyanogold* when merely vigorously rubbed undergoes "explosive" decomposition and *di-n-propylmonocyanogold* undergoes a similar decomposition when heated above its melting-point ( $94-95^\circ$ ), the decomposition taking place may be represented thus:



Free radicals, ethyl and *n*-propyl ( $R'$ ) are evolved and have been recognised (from the diethyl compound) as *n*-butane and (from the di-*n*-propyl compound) as *n*-hexane.

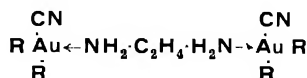
Compounds having the empirical formula  $RAuCN$  are almost insoluble in organic solvents and have high (and at present unknown) molecular weights; they are also produced from compounds of type (I) by long standing at the ordinary temperature (*cf.* Kharasch and Isbell, *loc.*). They are mixed aurous and auric compounds in which the aurous gold atoms are 2-covalent and the auric gold atoms are 4-covalent. In view of the fact that the four valencies of auric gold have a planar distribution, and that the two valencies of aurous gold have a linear distribution, the constitution of compounds having the empirical formula  $RAuCN$  cannot be represented by a planar ring structure which would also not be in keeping with their very low solubility. Their constitution can, however, be satisfactorily represented by a zig-zag chain structure:



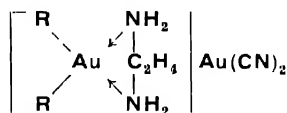
Such a constitution is in keeping with their insolubility and, unlike the parent substance,

with their having no melting-points. Further and complete loss of hydrocarbon radicals results in the production of aurous monocyanide (aurous cyanide) which, as pointed out above, probably possesses a straight chain structure (Gibson, Proc. Roy. Soc. 1939, A, 173, 160).

Compounds of type (I) yield ethylenediamine derivatives having the general formula



These are colourless crystalline non-electrolytes. When suspended in water and the mixture heated, solution takes place gradually; free radicals—identified as the corresponding hydrocarbons—are evolved initially, and the clear solution yields after evaporation a colourless crystalline salt having the formula

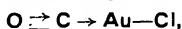


These aurocyanides of type IV may also be obtained by boiling benzene solutions of compounds of type III and recrystallising the resulting solid products from water. On treatment with sufficient mineral acid to combine with the ethylenediamine they are converted into the compounds having the empirical formula  $RAuCN$ , type II.

The "phenylauric chloride," having the formula  $PhAuCl_2$  and m.p.  $73-75^\circ$ , which has been described by Kharasch and Isbell (J. Amer. Chem. Soc. 1931, 53, 3055) and which was prepared by the addition of auric chloride to an excess of pure benzene, does not appear to have either a constitution or properties analogous to those of the monoalkyldibromogold compounds (*cf.* J.C.S. 1934, 862; 1935, 1024 (footnote)). If such a compound does exist  $PhAuCl_2$  would only represent its empirical formula. The compounds prepared similarly from toluene, diphenyl (decomp. at  $65^\circ$ ) and methyl salicylate (m.p.  $107^\circ$  decomp.) contain a molecule of water in each case even after recrystallisation from ether.

The compound *aurous chloride carbonyl*, classified by Kharasch and Isbell (J. Amer. Chem. Soc., 1930, 52, 2919) as an organic gold compound, was first prepared by Manchot and Gall (Ber. 1925, 58 [B], 2175) by passing carbon monoxide over gold trichloride at  $95^\circ$ . Kharasch and Isbell prepared it from aurous chloride in benzene suspension ( $20-30^\circ$ ) and from gold trichloride in tetrachloroethylene ( $100-140^\circ$ ). It is a colourless substance soluble in organic solvents and decomposed by water. Its molecular weight is normal in freezing benzene and the compound dissociates in hot solvents and when heated under reduced pressure yielding

pure aurous chloride. It is suggested that its constitution should be expressed,



in keeping with the 2-covalency of aurous gold and with the linear distribution of the two valencies. With pyridine and hexamethylene-tetramine carbon monoxide is evolved and (presumably) co-ordination compounds of aurous chloride (*e.g.*  $\text{H}_6\text{C}_6\text{N} \rightarrow \text{Au}-\text{Cl}$ ) are formed.

Aurous chloride carbonyl reacts with aryl-magnesium halides giving good yields of bis-aromatic hydrocarbons (diphenyl, di-*o*-tolyl, di-*p*-tolyl, dibenzyl, *aa'*-dinaphthyl), carbon monoxide being evolved and gold precipitated.

C. S. G.

**GOLD, MANNHEIM.** A brass containing 80% copper and 20% zinc.

**GOLD, MOSAIC.** A fine, flaky, yellow form of stannic sulphide which is now used only to a limited extent to imitate bronze. It is prepared by gently heating a mixture of 7 parts of sulphur, 6 parts of ammonium chloride and 18 parts of a powdered amalgam containing 12 parts of tin to 6 parts of mercury, until the odour of sulphuretted hydrogen is no longer perceptible. The residue is then heated to low redness and a mixture of mercurous chloride, ammonium chloride and cinnabar sublimes, while the mosaic gold alone remains. A good product is also obtained by heating a mixture of 5 parts of stannous sulphide and 8 parts of mercuric chloride.

A pale yellow mosaic gold is produced by heating 50 parts of crystalline stannous chloride with 25 parts flowers of sulphur; a reddish-yellow product is obtained on heating together 50 parts 50% tin-amalgam, 25 parts stannous chloride, 35 parts ammonium chloride and 35 parts of sulphur (Lagutt, *Z. angew. Chem.* 1897, 11, 557). The temperature used should not be too high, as the stannic sulphide, when strongly heated, loses one equivalent of sulphur and becomes black.

Mosaic gold is insoluble in nitric and hydrochloric acid, but dissolves in *aqua regia* and in alkaline hydroxides.

A brass containing 52-55% zinc has also been known by this name.

C. O. B.

**GOLD NUMBER** (*v.* Vol. III, 287b).

**GOLD PURPLE** (*Purple of Cassius*).

This product consists of a mixture of metallic gold and tin oxide. An imperfect description of its preparation was given by Andreas Cassius ("De Auro," 1685). It is obtained as a fine flocculent purple precipitate on addition of a solution of stannous chloride, which contains some stannic chloride, to a dilute neutral solution of gold chloride. The presence of stannic chloride is essential as pure stannous chloride produces only a brown precipitate. T. K. Rose (*Chem. News*, 1892, 66, 271) has shown that the formation of the colour is capable of detecting 1 part of gold in 100,000,000 parts of water when the test is carried out under specific conditions.

A very fine product is obtained by adding stannous chloride to ferric chloride until the solution is of a pale green colour and employing

this mixture to precipitate the gold from solution. R. Zsigmondy (*Annalen*, 1898, 301, 361) prepared Purple of Cassius by mixing 200 c.c. gold chloride solution (3 g. Au per litre) and 250 c.c. stannous chloride solution (3 g. Sn per litre) with a very slight excess of HCl and 4 litres of water. After 3 days the purple was deposited, leaving a liquid free from gold and tin. The precipitate thus prepared contained, after ignition, 40-3% gold and 59.7% stannic oxide.

According to H. Moissan (*Compt. rend.* 1905, 141, 977), when gold-tin alloys, mixed with lime, are distilled in air, a finely divided mixture of stannic oxide, lime and gold is obtained having the colour and properties of Purple of Cassius. Similar deposits of varying tint can be obtained by substituting for lime other oxides such as zirconia, silica, magnesia or alumina.

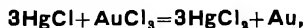
Purple of Cassius may also be obtained in great beauty by treating an alloy of gold 2 parts, tin 3.5 parts and silver 15 parts with strong nitric acid to dissolve the silver and oxidise the tin (Müller, *J. pr. Chem.* 1884, [ii], 30, 252). E. A. Schneider (*Z. anorg. Chem.* 1894, 5, 80) obtained gold purple by treating an alloy of gold, tin and silver with concentrated nitric acid. The resulting black powder was washed with ammonia when a ruby-red coloured solution was obtained which was dialysed until it contained no more ammonia. Potassium cyanide decolourises this solution and stannic oxide separates. With mercury, the solution becomes brownish-red and gold is extracted; with excess of hydrochloric acid, the solution becomes violet and yields finely divided gold on dialysis. According to this author, the soluble form of purple gold is possibly a mixture of the hydrosols of gold and stannic acid.

Purple of Cassius is used in the manufacture of artificial gems (*v.* Vol. V, 513c), and for imparting a red, rose or pink colour to glass, porcelain or enamel; it varies in colour from a violet to a purplish-red or brown.

In the dry state, gold purple is insoluble in either strong or dilute alkalis, but when moist it dissolves in water in the presence of very small quantities of alkalis. Salts and excess of acids and alkalis precipitate the purple from these solutions. Whilst moist, it is also soluble in ammonia with the production of a purple colour from which the precipitate is redeposited on addition of an acid or on boiling, and in the latter case is not again soluble. The ammoniacal solution precipitates gold on exposure to light. The purple does not pass through the membrane of a dialyser.

When dried and triturated, the Purple of Cassius acquires a metallic lustre, but no gold is removed from it by the action of mercury. It retains water at 100°, but gives it up and acquires a brick-red colour when ignited, and loses its colour at the melting-point of gold without the evolution of oxygen.

On adding a greater quantity of mercurous chloride to a solution of auric chloride than that required for the reaction:



the characteristic colour of Purple of Cassius is obtained. If barium sulphate suspended in



water is previously mixed with the mercurous chloride, the sulphate takes up the gold and acquires the purple colour. Antony and Lucchesi (Gazzetta, 1896, 26, ii, 195) therefore regarded true Purple of Cassius as being not a compound but merely stannic oxide mechanically covered with gold.

M. Muller (*l.c.*) also prepared purples by several processes without the use of tin. A pale rose (containing 0.1% gold) to deep carmine pigment is produced by igniting a well washed and dried mixture of magnesium oxide and gold chloride. A similar result is obtained by heating the mixture in a current of hydrogen. Lime, calcium carbonate, calcium phosphate, barium sulphate and lead and zinc oxides give similar but less satisfactory results.

The most intense purple is obtained by treating a mixture of aluminium hydroxide and gold chloride with grape-sugar solution. The mixture is agitated and heated until of a bright scarlet colour, but the colour must not be allowed to reach a purplish-red or the resultant product will be of inferior brilliancy.

Similar purples, but less brilliant than those with magnesia and alumina are obtained with tin: 11.5 g. of stannous chloride are dissolved in 200 c.c. of water, gold chloride added and the solution rendered alkaline by the addition of potassium carbonate. Grape-sugar solution is now added and the mixture is diluted to 300 litres and is then warmed until of the required colour.

C. O. B.

"GOMENOL." A trade name for an essential oil prepared from the leaves of *Melaleuca viridiflora* Linn. (Fam. Myrtaceae), found in New Caledonia. It is similar to, if not identical with, oil of cajuput (*q.v.*).

C. T. B.

**GONDANG WAX** (? Getah Wax). A wax recovered from the latex of the Javanese wild fig-tree (*v. Vol. V, 171b*).

**GOND BABUL** (*v. Vol. I, 585a*).

**GONIOMETER.** The goniometer is an instrument for measuring the angles between faces in crystals. The constancy of the angle between corresponding faces in different crystals of the same substance is the most striking feature of obviously crystalline matter and was, naturally, the first to be studied quantitatively.

In crystalline matter the atoms or molecules are arranged in a regular pattern in three dimensions. Many crystalline substances develop external faces, the presence of which was commonly taken to be the distinguishing mark of the crystalline state but which we now know is not essential. But when a crystal has external faces these are parallel to planes of atoms in the structure so that the external faces are regularly arranged and define the internal regularity of construction of the crystal. Because of this symmetry the faces lie in zones, groups of faces in a "zone" being all parallel to a direction which is called the zone-axis. The measurement of the angles between faces is of fundamental importance in the study of the symmetry of crystals and is of great help in their identification.

The Contact Goniometer was invented by Carangeot in 1780 and was used by the crystallo-

graphers Romé de l'Isle and the Abbé Haüy. It consists of a semi-circular protractor graduated in degrees, with a straight bar pivoted at the centre. With this instrument it is possible to measure the angle between faces only if these are fairly large.

In 1809 Wollaston invented the Reflecting Goniometer, the principle of which is used in modern instruments although these have been greatly improved. The reflection of a fixed image is obtained over a reference mark from two faces in turn, and the angle through which the crystal is turned between the two reflecting positions is the angle between the normals to the two faces in question.

The crystal is mounted on a holder consisting of two movable arcs perpendicular to each other. It is so adjusted that one prominent face is parallel to the plane of one of these arcs. The arcs are then tilted until the zone-axis of the one to be measured is parallel to the axis of the goniometer, *i.e.* perpendicular to the graduated disc. A fairly parallel beam of light from a distant source or from a collimator is reflected from the prominent face previously mentioned, and the crystal is set so that this reflected image lies over a fixed reference mark. The plane containing the incident and reflected beams and the normal to the face must therefore be parallel to the plane of the graduated disc. This procedure is repeated with another face using only the adjusting arcs which will move the original face only in its own plane. In this way the crystal can be quickly adjusted so that the zone-axis of the zone to be measured is set parallel to the axis of the instrument. As the graduated disc is turned through 360° the settings at which reflection occur for the various faces in turn are noted.

The usual procedure is as follows:—

(1) A drawing of the crystal with lettered or numbered faces is made as it is essential to be able to recognise each face.

(2) The crystal is set up with a zone-axis parallel to the axis of the instrument as described.

(3) The angles between the normals to faces in this zone are measured, the readings being set out as below:

Face	Quality of Image	Reading	Differences of Pairs of Readings
------	------------------	---------	----------------------------------

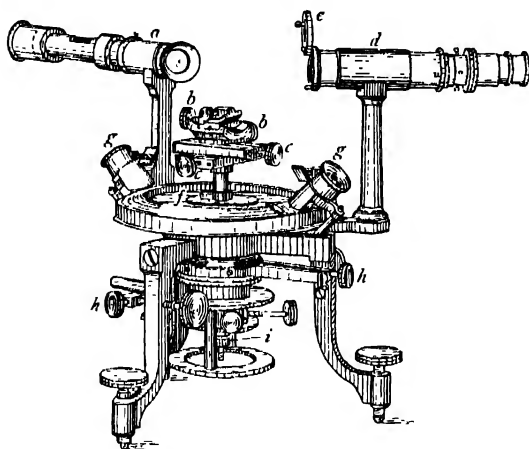
(4) This process is repeated with other zones until sufficient data have been obtained to allow the directions of the normals to each face to be plotted on a projection (nearly always the stereographic).

(5) A consistent set of indices is assigned to the faces, and the forms present are noted. The axial ratio or morphological constants of crystals can be obtained after some simple calculations.

Although all Reflecting Goniometers employ the same principle, they are of different types. In the simplest Student's Goniometer the image of a distant source of light is used because the light must be as nearly parallel as can be obtained. This image is reflected from a fixed mirror and this provides a reference mark, while

the image reflected from the crystal can be seen at the same time because the crystal is small compared with the mirror. The tilting adjustments carried on the graduated disc are very simple.

More accurate goniometers are fitted with collimators so that a fairly parallel beam can be obtained from a near source. They have also a telescope, the cross-wires of which provide the most accurate reference mark. Such goniometers are of two types, Vertical Circle or Horizontal Circle. Vertical Circle Goniometers are cheaper but Horizontal Circle goniometers have definite advantages; the crystal is much less likely to shift in the wax mount under its own weight and thus larger specimens can be measured, the large amount of possible movement of the telescope makes it easier to deal with difficult cases and also allows the instrument to be used for the determination of refractive indices as well as of crystal angles. A very good type of Horizontal Circle Goniometer is illustrated in the figure below.



NO. 2A FUESS REFLECTING GONIOMETER.

- |   |                    |
|---|--------------------|
| a. Collimator.                                    | b. Tilting screws. |
| c. Centering screws.                              | d. Telescope.      |
| e. Lens for changing telescope into a microscope. |                    |
| f. Disc bearing graduated circle.                 | h. Fixing screws.  |
| g. Vernier microscopes.                           |                    |
| i. Height adjusting screw.                        |                    |

The accuracy with which angle measurements can be made depends both on the instrument and on the crystal. The type of instrument illustrated can be read accurately to half-minutes. In the case of very good crystals this order of accuracy is required, although even these will show differences of as much as a whole minute owing to irregularities in crystal growth. But even greater accuracy is required in the study of the change of angle with change of temperature, which is one way of determining the coefficient of thermal expansion of a crystal. For this type of work a larger Horizontal Circle Goniometer, such as the Fuess No. 1a, which can be read to seconds is constructed. Crystals vary from very good ones suitable for such accurate measurement down to very bad ones

in which the irregularities of growth are such that the reflected image extends over two or three degrees.

Although a good Horizontal Circle Goniometer such as that illustrated is adequate for nearly all crystallographic work, more complicated two- and three-circle instruments have been developed in the last 50 years by Federov, Czapski, V. Goldschmidt and Herbert Smith. These have the advantage that the crystal is set up once only and in cases where there are a large number of very small faces difficult to identify, this is useful. Of course only one zone can be measured through 360°, but this is not a serious disadvantage as crystals rich in faces are often those which have been attached by one end to a surface during growth and so have only one end well developed. Both the practical and mathematical techniques required for handling these Theodolite Goniometers with two or three circles are much more complicated than for the single circle instrument. But it must be emphasised that for almost all goniometrical purposes in

mineralogical and chemical laboratories the single circle instrument is entirely adequate and, also, that the technique of using it is easily learned. A very full description of the various types of instruments and of their use, with practical examples, is given by A. E. H. Tutton in "Crystallography and Practical Crystal Measurement," 2 Vols., 1922 (Macmillan & Co.).

In the course of the last century mineralogists have built up a vast collection of data on the forms, angles and symmetry of minerals. The corresponding data for crystals of organic and of inorganic compounds which do not occur as minerals are very scanty. Such data are useful in the rapid identification of crystalline substances and a good goniometer should be a valued piece of apparatus in every chemical laboratory.

N. F. M. H.

**GOOSEBERRY.** The fruit of *Ribes grossularia* (European species) or of *R. hirtellum* (*R. oxycanthoides*), the American gooseberry. The latter species produces reddish fruit, smaller than that of European species. Among

recorded percentage analyses of European gooseberries the following are typical:

	—1 <sup>1</sup>	11 <sup>2</sup>
Total solids	12.0	11.9–15.1
Acid . . .	1.95*	1.5–2.3†
Invert sugar	4.87	—
Sucrose . .	0.18	0.10–0.12
Glucose . .	—	1.2–3.6
Lævulose . .	—	2.1–3.8
Ash . . .	0.43	

(1) (Z. Unters. Nahr. u. Genussm. 1910, 19, 558.  
Hotter (Z. landw. Versuchsw. Deut.-Oesterr. 1906,  
9, 947.  
As citric acid.  
As malic acid.

Windisch and Schmidt (Z. Unters. Nahr.-

Genusm. 1909, 17, 584) give the average percentage composition of gooseberry juice as:

Total solids.	Acid (as citric).	Invert sugar.	Sucrose	Tannin.	Ash.
11.05	0.32	1.16	6.58	0.38	0.08
				0.08	0.42

In earlier analyses the free acidity of gooseberry juice was regarded as due almost entirely to malic acid. It would appear, however, that citric acid in comparable proportions is also present. Thus Bigelow and Dunbar (Ind. Eng. Chem. 1917, 9, 762) report 1.72–2.63% of citric acid and 0.28–2.08% of malic acid in American species, and Muttelet (Ann. Falsif. 1922, 15, 453) finds 2.07% of citric acid in red and 2.20% in white European varieties.

Gooseberries are notably rich in vitamin C, Kudrjavzeva and Ivanova (Voprosi Pitaniya, 1935, 4, 114) recording as much as 500 units per kg. of berries, i.e. of the same order as in oranges and lemons.

The composition of gooseberry ash is given by Wolff as:

Total ash	H <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>
0.38	0.15	0.04	0.05	0.02	0.07	0.02	0.01

expressed as percentage of the fresh fruit. According to Dodd (Analyst, 1929, 54, 15) the dry matter of the fruit contains 0.028% of boric acid.

A. G. Po.

**GORLI SEED OIL** (v. Vol. II, 523b).

**GORLIC ACID** (v. Vol. II, 523b).

**GORSE, FURZE or WHIN.** *Ulex europaeus* L. A leguminous shrub common on poor dry heath soils. The leaves develop as spines. The tender young shoots are readily eaten by cattle and horses as also is the older, harder growth after suitable crushing (Voelcker, J. Roy. Agric. Soc. 1899 and 1901). Other species, *U. nanus* and *U. gallii*, also occur in Britain. In some areas gorse is cultivated, more especially as a horse fodder, for which purpose its food value is approximately 40% of that of hay.

Girard (Ann. Agron. 1901, 27, 5) records the percentage composition of gorse as:

Water	Protein.	Fat.	N-free extract.	Cellulose	Ash.
52.7	4.6	0.9	26.0	14.5	1.6

The N-free extract includes sugars 1.4, pennisins 9 and pectin 1.6%. The ash contains:

H <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>
27.1	11.7	4.3	2.4	6.7	4.7

An alkaloid, "ulexine," obtained from the seeds by Gerrard (Pharm. J. 1886, [III], 17, 101, 229) is identical with cytosine (*q.v.*) (Partheil, Ber. 1891, 24, 634). From the flowers Bridel and Beguin (Bull. Soc. Chim. biol. 1926, 8, 915) have isolated a glucoside, ulexoside, hydrolysable to invert sugar and ulexogenol.

A. G. Po.

**GOSIO GAS** (v. Vol. I, 479d, 483c).

**GOSLARITE, Zinc Vitriol or White Vitriol.**

Hydrated zinc sulphate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , crystallised in the orthorhombic system and isomorphous with epsomite. It results from the weathering of zinc-blende, and usually forms

white encrusting masses, or sometimes aggregates of fine, silky fibres. Being readily soluble in water it is not of common occurrence, but is occasionally found in the old galleries of zinc mines. Considerable quantities were at one time obtained from the Rammelsberg mine near Goslar in the Harz Mountains. Varieties are *erro-goslarite* and *cupro-goslarite*.

L. J. S.

**GOSSIPETIN** (v. Vol. III, 405b).

**GOSSIPITONE** (v. Vol. III, 405d).

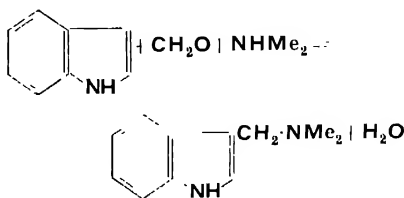
**GOSSIPITRIN** (v. Vol. III, 406b).

**GOSSIPOL** (v. Vol. III, 407d).

**GOULARD'S EXTRACT, LOTION, WATER.** Solutions of basic lead acetate.

**"GRAHAM'S SALT,"** sodium hexameta-phosphate (v. CALGON).

**GRAMINE**,  $\text{C}_{11}\text{H}_{14}\text{N}_2$ , is a crystalline base discovered in certain chlorophyll-defective mutants of barley by Von Euler and Hellstrom (Z. physiol. Chem. 1932, 208, 43; 1933, 217, 23); the yield was about 0.01% of the dry weight of the plants. The same base was next described as the alkaloid *donaxine*, which Orechhoff and Norkina (Ber. 1935, 68 [B], 436) isolated in a yield of 0.57% from the reed *Arundo donax* from Central Asia; Madinaveitia (J.C.S. 1937, 1927) obtained 0.28% from the same species growing on the coast near Barcelona. The constitution was investigated by Von Euler, Erdtman and Hellstrom (Ber. 1936, 69 [B], 743) but only fully established as 3-dimethyl-ammomethylindole by synthesis (Th. Wieland and Chi Yi Hsing, Annalen, 1936, 526, 188; Kuhn and Stein, Ber. 1937, 60 [B], 567). The second synthesis, a condensation of indole with formaldehyde and dimethylamine in the cold, is probably biological and gives a quantitative yield:



Gramine forms needles from acetone, m.p. 134°; *picrate*, m.p. 141°; *perchlorate*, m.p. 150°. Orechhoff and Norkina describe a *methiodide*, m.p. 177°, but a "methiodide" melting above 350° and obtained by Wieland and Chi Yi Hsing, as well as by Kuhn and Stein, was in all probability tetramethylammonium iodide. Madinaveitia showed that in the presence of methyl iodide and potassium hydroxide in methanol solution, gramine is quantitatively decomposed into 3-methoxymethylindole and tetramethylammonium iodide, and that, without alkali, the latter salt is also formed (along with 3-hydroxymethylindole?). Ethyl iodide reacts normally with gramine in neutral solution, but in alkaline solution dimethylethylamine is formed.

*Arundo donax* contains also a minute quantity of *donaxarine*,  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2$ , m.p. 217° (Madinaveitia). This second alkaloid is an indole substituted in the 2-position, for it gives neither the

Ehrlich nor the Hopkins and Cole reaction (both positive with gramine). Donaxarine contains one —NMe group, but no —OMe or —CMe, and is optically inactive.

## G. B.

**GRANITE.** An acid igneous rock consisting of a granular (hence the name) holocrystalline aggregate of quartz, feldspar and mica. It contains about 65–75% of silica, which is present partly as free silica (quartz forming 30–50% of the rock), and partly in combination in the silicates. The feldspar (36–68%) is generally a potash-feldspar, usually orthoclase, but sometimes microcline: it may also, especially in the “soda-granites,” be a soda-bearing orthoclase, anorthoclase or a plagioclase (albite to oligoclase). The mica (5–18% of the rock) is usually of two kinds, a white mica, muscovite, and a black mica, biotite.<sup>1</sup> The one-mica granite, biotite-granite, is sometimes distinguished as *granitite*. Less frequently, hornblende or augite may partly or wholly take the place of mica, as in hornblende-granite and augite-granite. In other varieties, especially those altered by pneumatolytic agencies, tourmaline may be present. Granites differ widely in their general appearance and character, owing to variations in their coarseness of grain, the occasional presence of larger porphyritic crystals embedded in a finer-grained groundmass, the colour of the felspars (dull white to pink), and the lack or predominance of the dark-coloured minerals, biotite and hornblende. Sp.gr. 2.6–2.8; weight per cu. ft., 160–175 lb.; crushing strength, 1,000, 2,000, 3,000 tons per sq. ft. Degree of porosity very low, 0.2–0.3%. The grain of the rock is sufficiently coarse for the individual minerals to be distinguishable by the unaided eye. It varies from fine-grained in *aplite* (a variety composed only of quartz and feldspar) to very coarse-grained in *pegmatite* and *graphic granite* (the latter characterised by an intimate intergrowth of quartz and feldspar). At times granite displays a more or less pronounced foliated structure (gneissose granite), passing imperceptibly into *gneiss*. This rock has the same mineral and chemical composition as granite, and to a certain extent can be employed for the same purposes.

The following analyses are of: I, Coarse-grained, red biotite-granite from Peterhead, Aberdeen (J. A. Phillips, 1880). II, Fine-grained, bluish-grey muscovite-biotite-granite from Rubislaw, Aberdeen (W. Mackie, 1901). III, Biotite-granite with large porphyritic crystals of red feldspar from Shap, Westmorland (J. B. Cohen, 1891). IV, Grey muscovite-biotite-granite from Greedy, near Luxullian, Cornwall (J. A. Phillips, 1880). V, Dark red, medium-grained hornblende-biotite-granite from Mount Sorrel, Leicestershire (C. K. Baker). VI, Average of nine analyses of the grey, two-mica granites, of Leinster, S.E. Ireland (S. Haughton, 1855). For a large collection of analyses of granite, v. J. Roth, “Beitrag z. Petrographie d. plutonischen Gesteine”, Berlin,

1873–84; H. S. Washington, U.S. Geol. Survey, Prof. Paper, 1917, No. 99.

	I.	II.	III.	IV.	V.	VI.
SiO <sub>2</sub>	73.70	69.01	68.55	69.64	67.16	72.08
Al <sub>2</sub> O <sub>3</sub>	14.44	17.74	16.21	17.35	16.19	14.46
Fe <sub>2</sub> O <sub>3</sub>	0.43	0.97	2.26	1.04	3.82	2.40
FeO	1.49	2.05	n.d.	1.97	—	—
MnO	trace	—	0.15	trace	—	—
MgO	trace	0.48	1.04	0.21	1.58	0.10
CaO	1.08	1.95	2.40	1.40	2.59	1.76
Na <sub>2</sub> O	4.21	2.73	4.08	3.51	2.43	3.01
K <sub>2</sub> O	4.43	3.94	4.14	4.08	5.38	4.80
P <sub>2</sub> O <sub>5</sub>	trace	—	—	trace	—	—
H <sub>2</sub> O	0.61	1.18	n.d.	0.72	1.02	0.91
Sp gr.	100.39 2.60	100.05 2.61	99.13 2.60	99.92 2.72	100.17 2.66	99.52 2.63

Granites are of wide distribution as rock-masses of considerable magnitude. They are extensively developed and quarried in Cornwall and Devon, where they occur as a series of bosses protruding through the hills or clay-slate. The largest of these intrusions are, proceeding westwards, those of Dartmoor, Brown Willy or Bodmin Moor, St. Austell or Hensbarrow, Carn Menlez or Penryn and the Land's End or Penzance districts. In addition to these principal exposures there are numerous smaller masses. The granite of Devon and Cornwall is usually grey and coarse-grained, but red granite also occurs, as at Trowlesworthy in the western part of Dartmoor. Although used locally since prehistoric times, Cornish granites were not systematically quarried until early in the eighteenth century; one of the first quarries to be developed was the De Lank quarry near Bodmin, which supplied the material for the exterior of the Eddystone Lighthouse in 1756. Dartmoor granite was sent to London in 1817 for the construction of Waterloo Bridge, and in 1831 for London Bridge. The granites of Scotland are of great industrial importance. Aberdeen granite was first brought to London for paving in 1764, but the great development of the trade dates from about 1850. The Aberdeen stone, valued for monumental work, is of a grey or blue tint, whilst that of Peterhead is usually of a fine pink colour. The Ross of Mull in Argyllshire furnishes a handsome pink granite, yielding blocks of exceptional size. Granite is also quarried in Kirkeudbrightshire, the grey stone of Dalbeattie being well-known in commerce. Ireland is rich in granites. The very large Leinster mass, in the counties of Dublin, Wicklow, Wexford and Carlow was quarried as early as 1680. Other important occurrences are in the Mourne Mountains in Co. Down, and in Co. Galway and Co. Donegal. Other British occurrences are in the Scilly Islands, Jersey and Guernsey, Lundy Island, Malvern Hills, Mount Sorrel in Leicestershire, Skiddaw, Eskdale, and Shap in the Lake District, the Sarn district in North Wales, and Foxdale and Dhoo in the Isle of Man; and in Scotland many other localities in addition to those mentioned above.

Granite is extensively used as a building and paving stone, and owing to its massive character and durability it is especially useful

<sup>1</sup> These minerals carry part of the potash, each of them containing about 10% K<sub>2</sub>O. The bulk of the potash is, however, carried by the felspar, pure potash-feldspar containing 16.9% K<sub>2</sub>O.

where massive constructive work is required, as in the foundation of buildings, in docks, seawalls, piers of bridges, lighthouses, etc. Taking a high polish, which is retained on exposure to weather, and being suitable for carving, it is much in demand for ornamental and monumental work. Refuse from the quarries is dressed as paving sets, or kerb stones, or crushed and screened for road metal, railway ballast and granite chips. Partly weathered granite from near the surface, especially when covered by a soil rich in humic acids, shows dull cloudy feldspars and the darker silicates have a rusty appearance, and the rock itself is often quite crumbly. This surface weathering may sometimes extend to considerable depths, and under certain conditions china-stone or china-clay may result. The solid fresh rock is, however, little affected by weathering processes when employed as a building stone. The most important cause of disintegration under these conditions is that due to the unequal degree of expansion and contraction of the different minerals with changes of temperature; coarse-grained granites are more affected by this agency than the finer-grained varieties. The handsome coarse-grained Rapakivi granite of Finland lacks durability on this account. Granite has further the defect that it does not resist fire well. The cracking and scaling of the surface is due to the presence in the quartz of vast numbers of microscopic cavities, containing water and liquid carbon dioxide. Stone containing nodules and specks of iron-pyrites should be avoided, since this mineral readily decomposes, producing free acid and unsightly brown stains. Of special varieties used for ornamental purposes mention may be made of *luxullianite*, and orbicular or spheroidal granite. The former, from Luxullian in Cornwall, consists of large porphyritic crystals of pink felspar set in a black matrix of tourmaline and quartz. A good set of large polished blocks and slabs of orbicular granite from several localities is displayed in the Mineral Gallery of the British Museum (Natural History). Granite was used as an ornamental stone by the ancient Egyptians and the Romans.

Granite rocks are always divided naturally by joints, which usually run in three directions, approximately at right angles, thus enabling the rock to be quarried in roughly cuboidal blocks. These are sometimes of considerable size, providing, for example, the obelisks up to 100 ft. in length obtained by the ancient Egyptians in the quarries of pink hornblende-biotite granite at Assouan (Syene) in Upper Egypt. The blocks are split up by "plug and feather" wedges, the splitting taking place more readily in certain directions, known to the quarrymen as the "rift" or "grain" of the stone. This is sometimes due to the presence of flow structure in the rock with a parallelism of the flakes of mica, but at other times it is apparently due to the effect of stresses. When the surface is required to be dressed smooth, it is "fine-axed" by continual tapping, at right angles to the face, with a special form of axe. Slabs are cut by diamond saws, and columns up to 8 ft. in diameter are turned in the lathe with diamond-set

tools. The polishing of granite is effected by cast-iron planes worked over the smoothed surface, first with sand and water, and then with emery, the final polish being given with putty powder applied on thick felt. In this way even elaborate mouldings are polished. The name granite is sometimes incorrectly applied as a trade-name to stones of other kinds, e.g. "black granite" to a gabbro or other dark-coloured igneous rock of granitic texture, "Petit granit" to a black Belgian marble spotted with white enclinites, "Mendip granite" to a limestone, and "Ingletton granite" to a conglomerate.

Veins of metalliferous ores frequently occur in connection with granite masses, either in the granite itself or at its junction with the surrounding rocks. Tin ore, in particular, is almost always found only in association with granite. The pegmatite veins occurring in connection with granite often carry various gemstones (tourmaline, beryl, etc.) and rare-earth minerals.

*References.*—G. F. Harris, "Granite and our Granite Industries," London, 1888. J. Watson, "British and Foreign Building Stones," Cambridge, 1911. J. A. Howe, "Geology of Building Stones," London, 1910. G. P. Merrill, "Stones for Building and Decoration," 3rd ed., New York, 1903. J. G. C. Anderson and M. Macgregor, "The Granites of Scotland," Mem. Geol. Survey, 1939. On the granites of the eastern United States, see T. N. Dale, Bull. U.S. Geol. Survey, 1907, No. 313; 1908, No. 354; 1909, No. 404; 1911, No. 481.

L. J. S.

**GRANITE-APLITE** (v. Vol. III, 32d).

**GRANITE-PEGMATITE** (vol. III, 32d).

**GRAPE.** The fruit of *Vitis* spp. European varieties are normally derived from *V. vinifera* L. According to Winton, American varieties have been bred from *V. labrusca* L. (the fox grape), *V. aestivalis* Michx. (the summer grape) and *V. rotundifolia* Michx. (the Muscadine or southern fox grape). The famous American variety "Concord" is derived from *V. labrusca*. It is used for dessert and for the manufacture of grape juice, but is less favoured for the making of wine or of raisins. Typical analyses of the fruit include:

	H <sub>2</sub> O.	Protein.	Fat.	Fibre.	Carbohydrates.	Ash.
European (whole) <sup>1</sup>	79.1	0.7	—	2.1	16.9	0.5
European (skin) <sup>2</sup>	76.5	1.5	0.9	2.1	18.4	0.6
European (seeds) <sup>2</sup>	38.7	5.5	8.6	27.6	18.9	0.7
American (whole) <sup>3</sup>	77.4	1.3	1.6	2.2	17.0	0.5
American (skin and pulp) <sup>4</sup>	81.1	0.4	0.2	0.6	17.3	0.4
American (pulp) <sup>4</sup>	82.3	0.5	0.2	0.2	16.6	0.33

<sup>1</sup> König, "Analysis of Foods."

<sup>2</sup> Dalland (Rev. Intern. falsif. 1900, 13, 92).

<sup>3</sup> Atwater and Bryant (U.S. Dept. Agric. Off. Exp. Sta. Bull., No. 28 rev. (1906)).

<sup>4</sup> Miller and Hazzone (Hawaii Agric. Exp. Sta. Bull. No. 77 (1937)).

The composition of grape juice varies considerable with the stage of maturity of the harvested fruit and with growth conditions. Varietal differences may also be considerable. The storage quality and flavour of the fruit and the quality of preserved juice are largely controlled by the proportion of sugars and acids (mainly tartaric and malic) present in the juice. Among data for American varieties may be recorded the following percentage analyses of the juice:

	I.	II	III.
Total solids . . . . .	13.5-16.6	20.1	19.3-22.2
Protein . . . . .	0.7-0.4	0.4	0.27-0.45
Total acids (as tartaric acid) . . . . .	0.4-0.8	0.9	0.7-1.0
Tartarates (ditto) . . . . .	0.3-0.5	0.7	0.6-0.7
Invert sugar . . . . .	12.3-13.4	18.0	17.0-19.0
Sucrose . . . . .	0.0-1.0	0.0	0.0
Tannin . . . . .	0.03	0.06	0.1-0.4
Ash . . . . .	0.2	0.3	0.3

I. Varieties from *V. rotundifolia*, Gore (Ind. Eng. Chem. 1909, 1, 436).

II. Catawba variety from *V. labrusca*, Gore (*l.c.*).

III. Concord, Hartman and Tolman (U.S. Dept. Agric. Bull. 656 (1918)).

In juice from European varieties Colby reports variations in reducing sugar contents of 19.8-23.1%, in total sugars 21.0-23.5% and in free acids (as tartaric) 0.36-0.65%. Caldwell (J. Agric. Res. 1925, 30, 1133) in a study of the effect of growth conditions reports the analyses of 49 varieties of juice grown in the same locality during five successive seasons. Minimum and maximum percentage values obtained were:

Total solids . . . . .	12.9-26.0
Free acid (as tartaric) . . . . .	0.5-2.1
Invert sugar . . . . .	8.9-24.8
Sucrose . . . . .	0.0-5.6
Tannin . . . . .	0.03-2.4

In Muscadine grapes, which yield 3-5 gallons of juice per bushel, Armstrong *et al.* (Georgia Agric. Exp. Sta. Bull. 185, 3 (1934)) report the following ranges in juice characteristics: total solids 12.8-21.3%,  $pH$  3.42-2.96, tannins 0.02-0.417%.

During the ripening of grapes the juice composition shows a marked increase in sugar content and a diminution in acidity. Loss of acidity falls mainly on the malic acid: the total tartaric acid content is not greatly altered (Garino-Camina, Ann. Acad. Agric. Torino, 1914, 50, 233; Ferré, Ann. Falsif. 1928, 21, 75), although there is some conversion of free tartaric acid into tartrates (Brunet, Rev. vit. 1912, 37, 15). The ratio sugar/acid in the juice serves as a measure of ripeness of the fruit, complete ripeness corresponding to a ratio of 30 (Hugues and Buffard, Ann. Falsif. 1936, 29, 279) and commercial maturity with a ratio of 25 (Meurice and Boule, Bull. inst. agron. et sta. recherches Gembloux, 1935, 4, 22). Mathieu (Ann. Agron. 1937, 7, 249) states that juice of ripe dessert grapes should show a sugar/acid ratio of not less than 25 and  $d_{15}$  not below 1.070.

In Concord grapes Nelson (J. Amer. Chem. Soc. 1925, 47, 1177) found the acids of the juice to consist of *d*-tartaric (40%) and *l*-malic

acid (60%). Small proportions of citric acid, however, are reported by Hartmann and Hillig (J. Assoc. Off. Agric. Chem. 1928, 11, 257) and by Heiduschka and Pyriki (Z. Unters. Lebensm. 1929, 58, 378). The flavour of wine from northern grapes is said to be influenced by the presence of lactic acid in the fresh juice (Schindler and Hulač, Chem. Listy, 1929, 23, 73). Glyoxylic acid occurs in unripe fruit (Semichon and Flanz, Rev. vit. 1933, 79, 197) and a hexuronic acid (m.p. 165°) is reported in purple grapes by Cahill (Bull. Soc. Chim. biol. 1933, 15, 1462).

Fresh grape juice contains pectin and a partial clarification of the juice results from the action of enzymes of *Penicillium glaucum* which convert part of the pectin into soluble compounds and precipitate the remainder together with suspensoids (Willaman and Kertesz, New York Agric. Exp. Sta. Tech. Bull. 178, 181 (1931)). Barbera (Ann. tech. agrar. 1933, 6, No. 3, 1, 229, 350) isolated from grape juice a pectin yielding on hydrolysis arabinose, xylose, galactose, galacturonic acid and methyl alcohol. Its methoxyl content was less than that of orange pectin.

The odour of grape juice is ascribed to the presence of methyl anthranilate, of which 0.2-2.0 mg. per litre of juice is reported by Power and Chesnut (J. Amer. Chem. Soc. 1921, 43, 1741).

Unfermented grape juice is preserved commercially by pasteurisation or is concentrated by low-pressure distillation. In the latter condition it is sometimes referred to as grape "honey," an analysis of which is recorded by Caserio (Ind. ital. cons. aliment. 1930, 11, 51) as  $H_2O$  24, ether extract 0.7, ash 0.9, total sugars (as invert) 72, reducing sugars (as fructose) 66.8, protein 0.79, total acid (as malic) 1.5%. Gachot (Proc. 5th Intern. Cong. Tech. Chem. Agric. Ind. Holland, 1937, 11, 445) describes the pasteurised juice as having *d* 1.072, dry matter 19, sugars 15.6 and ash 0.29%.

The anthocyanin pigment of European grapes is  $\alpha$ -cyan,  $C_{25}H_{25}O_{12}Cl + 4H_2O$ , a monoglucoside of dimethyldephinidin ( $\alpha$ -idin) chloride,  $C_{17}H_{15}O_7Cl$  (Willstätter and Zollinger, Annalen, 1915, 408, 83; 1916, 412, 195). Anderson (J. Biol. Chem. 1923, 57, 795; 1924, 61, 97) isolated from Concord grapes a monoglucoside of the monomethyl ester of delphinidin. Both anthocyanin and anthocyanidin pigments were obtained from Italian grapes (Parisi and Bruini, Staz. sper. agr. ital. 1926, 59, 130).

GRAPE-SEED OIL (*q.v.*).

RAISINS and CURRANTS represent a wide range of varieties of dried grapes. Bornträger (Z. Unters. Nahr.-u. Genussm. 1899, 2, 257) gives the average percentage analyses of samples from several Mediterranean countries as:

Source.	$H_2O$ .	Acids.	Sugars	Ash.
Spain (muscatel) . . . . .	25.1	1.25	65.2	1.7
Italy (raisins) . . . . .	26.1	1.31	67.1	1.5
Palestine (raisins) . . . . .	22.7	1.22	69.8	1.5
Syria (raisins) . . . . .	—	1.0	61.8	1.8
Zanti (currants) . . . . .	—	1.4	66.0	1.7
S. Maura (currants) . . . . .	—	1.4	66.0	1.9

	Raisins.	Currants.
Water . . . . .	24.5	25.4
Nitrogenous matter . . . . .	2.4	1.2
Fat . . . . .	0.6	—
Free acid . . . . .	1.2	1.5
Invert sugar . . . . .	59.3	61.8
Sucrose . . . . .	2.0	—
Other carbohydrates . . . . .	1.3	5.9
Crude fibre and seeds . . . . .	7.0	2.4
Ash . . . . .	1.7	1.8

König's average data for raisins and currants are given in the table opposite.

Average analyses for the edible portion of American raisins are given by Atwater and Bryant (*l.c.*) as H<sub>2</sub>O 14.6, protein 2.6, fat 3.3, N-free extract and fibre 76.1, ash 3.4%.

RAISIN-SEED OIL (*v.* GRAPE-SEED OIL).

Recorded mineral analyses of grapes and their products include :

	Fresh fruit (European) <sup>1</sup>	Fresh fruit (Concord) <sup>2</sup>	Skin. <sup>3</sup>	Seed <sup>3</sup>	Juice <sup>3</sup>	"Honey." <sup>4</sup>
K <sub>2</sub> O . . . . .	0.19-0.35	0.22	0.40	0.28	0.25	0.19
Na <sub>2</sub> O . . . . .	0.01-0.06	0.004	0.03	0.03	0.01	—
CaO . . . . .	0.02-0.03	0.03	0.13	0.31	0.02	0.16
MgO . . . . .	0.01-0.02	0.21	0.03	0.08	0.02	—
Fe <sub>2</sub> O <sub>3</sub> . . . . .	—	—	0.12	0.005	0.006	0.003
Mn <sub>2</sub> O <sub>4</sub> . . . . .	—	—	0.005	0.003	0.02	—
P <sub>2</sub> O <sub>5</sub> . . . . .	0.08-0.18	0.04	0.16	0.22	0.05	0.61
SO <sub>3</sub> . . . . .	0.01-0.03	—	0.05	0.02	0.02	—
SiO <sub>2</sub> . . . . .	0.02-0.03	—	0.02	0.01	0.01	—
Cl . . . . .	0.00-0.02	0.001	0.005	0.003	0.004	—

Bioletti.

<sup>2</sup> Atwater and Bryant.

König.

Caserio.

Boric acid and traces of copper, aluminium and zinc have been reported by various observers.

A. G. Po.  
**GRAPEFRUIT.** The fruit of *Citrus decumana* Murr., sometimes described as *C. grandis* Osbeck or *C. aurantium* var. *grandis* L. The common grapefruit is grown widely in the tropical and subtropical areas of North America and of Africa. The "pomelo" is a pear-shaped variety with thick rind. In Hawaii a similar variety is known as the "shaddock." Winton ("Composition of Foods") quotes the percentage analyses (shown opposite) for the edible portions of the fruits:

	Grapefruit	Pomelo.	Shaddock
Water . . . . .	88.1	87.7	88.5
Protein . . . . .	0.6	0.7	1.2
Citric acid . . . . .	0.7	1.1	0.3
Total sugar . . . . .	6.6	9.2	8.1
Sucrose . . . . .	3.9	6.2	7.3
Ash . . . . .	0.43	0.63	0.49

Joachim and Pandittesekere (Trop. Agric. 1939, 93, 14) report analyses of grapefruit grown in Ceylon and quote comparative data for the juice of fruit from a number of sources :

	I. Florida	II. Trinidad	III. Puerto Rico.	IV. Texas.	V. S Africa	VI. Jamaica.	VII Ceylon.
Juice, % . . . . .				35.9-58.9	—	—	30.5-55.2
Citric acid, g./100 c.c. . . . .	0.9-1.4	1.0-1.1	1.1	1.0-1.4	1.5	0.8-1.5	0.9-1.9
Total solids, g./100 c.c. . . . .	6.9-9.7	8.6-9.2	8.1	8.3-10.5	—	9.8-11.8	7.0-10.7
Total sugars, g./100 c.c. . . . .	4.8-6.2	6.5-7.3	4.8	5.7-7.0			4.2-7.5
Reducing sugars, g./100 c.c. . . . .	3.4-4.0	4.8-5.1	3.1	2.3-3.2	4.6	—	2.1-4.0
Solids/acid . . . . .	7.2-7.8	8.3-9.0	7.1	7.7-9.0		7.3-13.3	4.6-8.9
pH . . . . .	3.0	3.1-3.3		3.2-3.3	3.4	—	3.3-4.0

- I. Roberts and Gaddum, Ind. Eng. Chem. 1937, 29, 574
- II, III. Hardy and Rodriguez, Trop. Agric. Trinidad, 1935, 12, 205.
- IV. Traub and Friend, Texas Agric. Exp. Sta. Bull. 1930, No. 419.
- V. Juritz, Union S. Africa, Dept. Agric. Sci. Bull. 1925, No. 40, 3.
- VI. Croucher, Jamaica, Dept. Sci. Agric. Bull. No. 5.
- VII. Joachim and Pandittesekere, *l.c.*

The pomelo juice is somewhat more concentrated, analyses showing an average of: solids 12.2, citric acid 2.5, total sugars 8.7, sucrose 5%.

In addition to citric acid smaller amounts of malic and traces of tartaric and oxalic acids occur in the juice. In Palestine fruit, Menchikow-

sky and Popper (Hadar, 1932, 5, 181) record: citric acid 0.67-1.15, tartaric acid 0.0003-0.0007, malic acid 0.007-0.016 and oxalic acid 0.002-0.005%.

Nelson and Keenan (Science, 1933, 77, 561) report 0.0028% of inosite in grapefruit juice.

During the ripening of grapefruit the ratio of sugar/acidity in the juice increases and is an approximate measure of maturity for commercial purposes. Hyatt (New Zealand J. Sci. Tech. 1936, 18, 409) considers the ratio of total solids (Brix) to acidity should be 5 or over in palatable fruit. Investigations of Zoller (Ind. Eng. Chem. 1918, 10, 364) and of Hawkins (J. Agric. Res. 1920, 20, 357; 1921, 22, 263) show that the change in sugar/acid ratio in normally ripening fruit is brought about by a relatively larger diminution in acid content than the increase in sugar. Storage of the fruit in warm conditions causes a marked increase in acidity with only a small change in sugar content, whereas during storage at 0° there is a considerable decrease in acidity, the sugar content again showing little change. There is a small increase in  $p_H$  of the juice during maturation, but the relationship is not sufficiently uniform to be of commercial interest (L. Smith, Florida Dept. Agric. Chem. Div. Rept. 1933/4, 85). Grapefruit juice is a rich source of vitamin C and also contains appreciable amounts of vitamin B. Its vitamin A content is small.

The bitter principle of grapefruit rind is the flavanone glucoside *naringin* which gives on hydrolysis *d*-glucose, *l*-rhamnose and *naringenin* (5:7:4'-trihydroxyflavanone). The amount present ranges from 0.14-0.8% of the weight of the whole fruit.

Steam distillation of the rind produces 1-5% of a yellow essential oil,  $n_D^{20}$  1.475-1.4785,  $d_4^{20}$  0.845-0.860, consisting of *d*-limonene 90-92, citral 3-5,  $\alpha$ -pinene 0.5-1.5, geraniol 1-2, and linalool 1-2%. The expressed oil from the rind, on distillation first *in vacuo* and then in steam, leaves 7.5% of a waxy residue (Nelson and Mottern, Ind. Eng. Chem. 1934, 26, 634). The wax contains solid fatty acids of molecular weight corresponding to  $C_{32}H_{64}O_2$ , together with linolenic, linoleic and oleic acids, a sapogenic ketone,  $C_{31}H_{62}O$ , m.p. 253°, hydrocarbons (mainly  $C_{29}H_{60}$  and  $C_{31}H_{64}$ ), a phytosterol,  $C_{28}H_{47}OH$ , m.p. 132°, and umbelliferone (Markley *et al.*, J. Biol. Chem. 1937, 118, 433). The pectin content of the peel frequently exceeds 10% of its total weight (*cf.* Poore, Ind. Eng. Chem. 1934, 26, 637).

The colour of grapefruit rind is due to a phlobatannin which darkens on exposure to air. Pink varieties contain lycopene and  $\beta$ -carotene (Matlack, J. Biol. Chem. 1935, 110, 249).

From grapefruit pulp Hiwatari (J. Biochem. Japan, 1927, 7, 169) has isolated glycine-betaine, stachydrine and putrescine.

Chace (U.S. Dept. Agric. Bur. Chem. Bull. 1904, No. 87) shows the ash of grapefruit to contain  $K_2O$  44.2,  $CaO$  7.3,  $MgO$  3.9,  $Fe_2O_3$  1.3,  $P_2O_5$  11.1,  $SO_3$  3.4 and  $Cl$  1.4%, the total ash content being 0.39% of the weight of the whole fresh fruit.

In recent years the rapidly extending canning process has led to the accumulation of much

grapefruit waste (peel, rag and seeds). Thomas (Citrus Ind. 1934, 15, No. 11, 8-9) reports this as being of value as a cattle food, its analysis being:

Water . . . . .	% 8.2
Protein . . . . .	4.9
Fibre . . . . .	11.9
N-free extract . . . . .	69.6
Ether extract . . . . .	1.1
Ash . . . . .	4.23

A. G. Po.

## GRAPEFRUIT, ESSENTIAL OIL OF

*v.* GRAPEFRUIT).

**GRAPE-SEED OIL (RAISIN-SEED OIL)** is obtained commercially from the residual pips recovered from the processing of the wine-grape (varieties of the old-world *Vitis vinifera* L., the American *V. labrusca*, *V. aestivalis* and *V. riparia*, and their hybrids) for the manufacture of wine or of seedless raisins (especially in California). The pips contain from 6 to 20% of oil, which may be recovered partially by expression, or in higher yield by extraction with solvents; the crude grape marc from the wine-pressing may be distilled as usual if desired before separating the pips. Since the first commercial trials in Italy in about 1770, grape-seed oil has been of occasional local importance (chiefly when other oils have been scarce) in many European wine-growing countries such as Italy, France, Germany, Austria and the Balkan States; recovery of grape seeds for oil manufacture was made compulsory in certain districts of Germany in 1938-39. The better qualities of the oil are used for edible purposes, whilst the lower grades may be employed for the manufacture of soap, paints, linoleum, etc. In California refined raisin-pip oil is used as an edible (salad) oil, for the coating of seeded raisins to prevent stickiness and for the manufacture of cosmetic preparations, as well as in the soap-making and paint and varnish industries (*v.* A. M. Paul, Food Ind. 1934, 6, 444; Eaton, Soap Trade Rev. 1937, 10, 497; Rabak, J. Ind. Eng. Chem. 1921, 13, 919; H. A. Gardner, U.S. Patent and Var. Manuf. Assoc. Scient. Sect. Circ. No. 190 (1923); H. Scheiber, Farbe u. Lack, 1936, 17, and later papers; Brambilla and Balbi, Chim. e. l'Ind. 1936, 18, 353; 1937, 19, 10; *see also* Bonnet, Bull. Soc. d'Encour. 1927, 126, 523 (review of French industry); Fritz, Chem.-Ztg. 1935, 59, 704 (German production)). Grape-seed oil is not satisfactory for the manufacture of Turkey red oils, nor as a lubricant; Margailan states, however, that blown grape-seed oil may be used for the latter purpose (Bull. Soc. d'Encour. 1927, 126, 560; Compt. rend. 1927, 185, 306).

Cold pressed grape-seed oil from fresh seeds is pale in colour and satisfactory in flavour; it is stated by Eaton, however (*see* Jamieson and McKinney, Oil and Soap, 1935, 12, 241), that both the freshly expressed crude oil and refined oils give a positive Kreis test. The technical oils vary in colour, acidity and taste according to the age and condition of the seed treated, but can be refined fairly easily.

The chemical constitution of grape-seed oil is still uncertain, as the data recorded for the oil



by various observers are very conflicting (cf. collected data in reviews by Fritz, *Seifens.-Ztg.* 1927, **54**, 704, and Balbi and Brambilla, *Olii Min.*, *Olii e Grassi*, *Colori e Vernici*, 1937, **17**, Nos. 3-7). The fact seems to be that the character of the oil varies widely from sample to sample; the variety of the plant (and there are supposed to be over 500 varieties of *V. vinifera*), the nature of the climate and of the soil are all factors which appear to influence the composition of the oil to a degree which is unusual among vegetable oils.

On the whole, the evidence suggests the existence of three main types of grape-seed oil.

(a) *The Hydroxylated or "Castor Oil" Type.*—The early investigator Horn (Mitt. Gew.-Mus. Wien, 1891, 185) and later Paris (Staz. sper. agr. ital. 1911, **44**, 669) reported iodine values of 94-96, saponification values of 178-179 and very high acetyl values, viz. 144.5 and 143, which were regarded as characteristic of grape-seed oil and indicative of the presence of glycerides of hydroxylated acids of the castor oil type. Considerable doubt has been cast upon the validity of these early results, as the methods employed for the determination of the acetyl value are open to adverse criticism; also in most cases the oils were highly acid and it has been found that some grape-seed oils, at least, are liable to develop high acetyl values upon ageing (cf. also Delaby and Charonnat, *Compt. rend.* 1930, **191**, 1011). Nevertheless, although such high acetyl values have never been observed again, the fairly recent examination of a large number of grape-seed oils of different origin by André (*ibid.* 1921, **172**, 1296, 1413; 1922, **175**, 107; 1923, **176**, 686, 843; André and Canal. *Bull. Soc. d'Encour.* 1927, **126**, 542; Taufel, Fischler and Jordan, *Allgem. Oel.-Fett-Ztg.* 1931, **28**, 119; cf. *Fettechem. Umschau*, 1934 **41**, 196) and Otin and Dima (*Allgem. Oel.-Fett-Ztg.* 1933, **30**, 71, 135; 1934, **31**, 107 cf. Beal and Beebe, *J. Ind. Eng. Chem.* 1915, **7**, 1034), seems to afford confirmation of the existence of a moderate amount of hydroxylated acids in certain grape-seed oils. Out of some 40 laboratory-prepared and 6 commercial samples studied by André, 6 had acetyl values between 20 and 50, whilst one—a commercial sample from Oran, having 40% free fatty acids—had an acetyl value of the order of 66. Most of the 40 Rumanian oils examined by Otin and Dima had hydroxyl values<sup>1</sup> in the region of 40 (equivalent to acetyl values of c. 39), the figure being somewhat higher (50-60) in a few cases. They give the following composition for an oil (iodine value 124, hydroxyl value 34.8) from Southern Bessarabia: hydroxy-acids 11.8% oleic acid 31.0%, linolic acid 43.7%, linolenic acid 0.14%, palmitic acid 6.2%, stearic acid 2.20%, glyceryl residue ( $C_3H_5$ ) 4.04%, unsaponifiable matter 0.59%.

Taufel reported hydroxyl values of 92 and 76 (equivalent to acetyl values of c. 86 and 71 respectively) for two oils of acid value 51 and 7 respectively: in both cases the fatty acid prepared by saponification had hydroxyl values

44-46 (acetyl values c. 45) which appears to confirm the existence of hydroxy-acids. Further evidence is supplied by André (*l.c.* 1921, 1923) who claims to have separated a mixture of a saturated and an unsaturated hydroxy acid ( $C_{18}$  or  $C_{16}$ ?) from a sample having an acetyl value of 49. Ricinoleic acid itself, however, is not present.

It must be noted that all these recent specimens had iodine values between 124 and 142 mostly between 132 and 139) and saponification values between 186 and 192 (most 189-190), and it seems likely that the low iodine values found by Horn and Paris were a consequence of the oxidation of the oil, since it has been shown by Otin and Dima that the iodine value falls very considerably when grape-seed oils are stored in the presence of air. No correlation can yet be drawn between the acetyl value and the variety of the grape or ecological factors; there can even be considerable variation in the acetyl value of oil from seeds harvested in the same vineyard in successive seasons (André), but it appears on the whole that a hot dry climate and a dry lime soil favour the production of hydroxy-acids.

It is doubtful whether oils having acetyl values in the region of 18-25 (cf. Fachini and Dorta, *th. Int. Congr. Appl. Chem.* 1909, Sect. IV, A 1, 28; André, *l.c.*; Jamieson and McKinney, *l.c.*) should be included in this group or under (c) (below).

(b) *The "Erucic Acid" Type.*—The occurrence of erucic acid in grape-seed oils was reported by Fitz (Ber. 1871, **4**, 442, 910) and again by Paris (*l.c.*), but was disputed by subsequent investigators including dell'Acqua (*Ann. chim. appl.* 1914, **2**, 295) and Jamieson and McKinney (*Oil and Soap*, 1935, **12**, 241). Its presence, however, was again affirmed by Carrière and Brunet (*Compt. rend.* 1927, **185**, 1516) and by Mikšić and Režek (oil from the American hybrid vine "Noah" grown in Jugoslavia: *Bull. Soc. chim. Roy. Jugoslav.* 1930, **1**, No. 2, 32).

(c) *The Semi-Drying Type of Grape-Seed Oil* is undoubtedly the most common. Erucic acid is absent, and as a rule the acetyl value is very low, although technical oils may show fairly high acetyl values owing to the formation of free fatty acids, mono- and di-glycerides by partial hydrolysis. The iodine values generally run from 130 to 140 (André records a maximal figure of 157); the saponification values are normal (c. 190) and the oils exhibit moderate drying properties which render them suitable as partial substitutes for more unsaturated oils in the paint and varnish industries, etc. The composition of the fatty acids of a Californian raisin-seed oil (iodine value 129) of this type (acetyl value 18.8, acid value 0) is given by Jamieson and McKinney, *l.c.* (cf. Taufel *et al.*, *l.c.*) as follows: palmitic acid 6.3; stearic acid 2.9; oleic acid 33.5; linolic acid 52.7; linolenic acid 2.4%. Traces of arachidic acid and melissic acid (probably derived from the wax on the seed coats) were also present (cf. Balbi and Brambilla, *Olii Min.*, etc., 1937, *l.c. supra*; Kaufmann, *Kette u. Seifen*, 1938, **45**, 288). An oil (iodine value 137.8) examined by Kauf-

<sup>1</sup> The hydroxyl values were determined by Normann's method; the approximate equivalent acetyl values have been obtained by calculation.

mann and Fiedler (*ibid.* 1937, **44**, 286) contained 10.8% of saturated acids but no linolenic acid.

The phytosterols of grape-seed oil appear to consist chiefly of sitosterol with a small amount of a dextrorotatory sterol (Antoniani and Zanelli, *Atti. R. Accad. Lincei*, 1932, [vi], **15**, 284).

The residual seed-cake after expression or extraction of the oil is fairly rich in protein and potassium phosphate and may be employed as an animal feeding-stuff or as fertiliser. In the case of raisin-pips, 15% of tannins can be recovered after extraction of the oil, leaving a residue suitable for cattle-feeding (Rabak, *Bull. U.S. Dept. Agric. Bur. Plant. Ind.* **276** (1936)).

Hitherto it has been usual to separate the pips from the grape marc before recovering the oil. The fruit pulp, however, also contains a certain amount of fatty matter of a more saturated character, so that a mixed fat, of which about one-half is derived from the pips and the rest from the skins and pulp, can be obtained by treating the unseparated dried marc. Such a fat examined by M. de Girves (*Bull. Assoc. Chim. Suer.* 1937, **54**, 140) had m.p. 51°, saponification value 182, acid value 26.8, iodine value 118 and unsaponifiable matter 5% (Fachini, *Ind. Oli Min. e. Grassi*, 1939, **10**, 122; S. A. Fabr. Chim. Arenella, F.P. 635628).

E. L.

#### GRAPHITE (v. Vol II, 313d).

**GRAPHITIC ACID**, graphitic oxide, formed on oxidising graphite, e.g. by treating it with potassium chlorate in nitric acid (Broche, *Phil. Trans.* 1859, **149**, 249; O. W. Storey, *Trans. Electro-chem. Soc.* 1927, **53**, preprint) or in a nitric-sulphuric acid mixture (U. Hofmann, A. Frenzel and E. Csálán, *Annalen*, 1934, **510**, 34), or by electrolytic oxidation of graphite anodes (U. Hofmann and A. Frenzel, *Kolloid-Z.* 1934, **68**, 149).

Graphitic acid is a green-grey powder of composition approximating to  $C_{11}H_4O_6$ . It yields colloidal solutions on treatment with hot water and suffers complete disruption with evolution of water vapour, carbon monoxide and carbon dioxide on heating to 200°.

Attempts have been made to find a definite constitution and stoichiometric composition for graphitic acid (H. Thiele, *Z. anorg. Chem.* 1930, **190**, 145; *Kolloid-Z.* 1932, **58**, 129). On the other hand it has been described as an adsorption complex of graphite, water, carbon monoxide and dioxide. Recent chemical, X-ray and other physical determinations have led to a different view. It now seems established that graphitic acid is formed by the insertion of oxygen atoms between the laminae of graphite and may be termed a two-dimensional macromolecule. The X-ray and other physical evidence for this structure includes the molecular uni-dimensional swelling in polar solvents discussed by Bruins (*Rec. trav. chim.* 1935, **54**, 317). The chemical evidence for this conclusion is briefly: Graphitic acid may be reconverted into graphite by moderate heating (U. Hofmann and A. Frenzel, *Kolloid-Z.* 1932, **58**, 8); the carbon/oxygen ratio varies between 2.9 and 3.5 but oxygen is never expelled as such nor directly as water; further, oxygen may be replaced by sulphur yielding graphitic sulphide on reducing

with hydrogen sulphide (Hofmann, Frenzel and Csálán, *loc.*).

Graphitic acid has been used in the preparation of threads, films, etc., by evaporating colloidal solutions (G.P. 298605), which are reduced to graphite by phenylhydrazine vapour (G.P. 600768), and also as a binder for carbon and metal oxides in the manufacture of electric heating resistances (G.P. 512264).

**GRAPPIERS** (v. Vol. II, 135b).

**GRASS-CLOTHS** (v. Vol. III, 32b).

**GRASS LAND.** Attention has recently been directed to the high proportion of inferior grass land in Britain. R. G. Stapledon, "The Land, Now and To-morrow," Faber and Faber, 1935, discusses this aspect of our agriculture from a national point of view, and on the results, so far obtained, from the application of his research work to the Cahn Hill Improvement Scheme, Aberystwyth, has shown how each type of grass land can be improved up to the level of that next higher in the scale. In a further book entitled "A Survey of the Agricultural and Waste Lands of Wales," Faber and Faber, 1936, Stapledon and his colleagues have been able, on the basis of a botanical survey, to classify grass land and produce a map of the grazings of Wales. Amongst points of exceptional interest two are of outstanding importance: (1) good rye-grass grazings occupy only 16,000 acres or 0.4% of the agricultural area in Wales, and (2) *Agrostis* pasture and *Molinia-Nardus* moor together occupy 54.8% of the agricultural area. The 1,697,000 acres of *Agrostis* pasture probably represents the most easily improvable grass land.

The results of recent research into the possibilities of grass as a food for live-stock have opened up new problems in connection with grass land improvement. Earlier grass-land research dealt mainly with two aspects: the effect of fertilisers, especially lime and basic slag, and the production of new swards by sowing, mainly in the north of England and Scotland. Accounts of this work are available in the Guides to the experiments on the Northumberland County Council's farm, Cocker Park (King's College, Newcastle-on-Tyne), and the publications of the North of Scotland Agricultural College, Aberdeen.

Large areas of grass land have become so noticeably deficient in lime and phosphate that the basis of the Government's agricultural policy as approved by Parliament in the Agriculture Act, 1937, has been to subsidise the use of lime and basic slag.

**LIME-DEFICIENCY.**—In areas of acid soils, especially on Coal Measures and Millstone Grit, the main factor limiting grass land productivity is lime-deficiency. The effects of lime-deficiency in the soil are accentuated in industrial areas by smoke pollution, which has an indirect effect on the crop through the soil and a direct effect on the plant itself. An abnormal accumulation of sulphur compounds in soil and crop is noticeable under such conditions, and the effect is worst on perennial crops such as grass. The application of lime quickly increases the calcium content of the herbage, but a change in the botanical composition is slower in appearing in

permanent grass. It is usually more economical to plough out the old sward, incorporate lime with the newly turned soil, and re-sow.

**PHOSPHATE-DEFICIENCY.**—Most clay soils, but especially Boulder Clays, exhibit serious phosphate-deficiency when under grass. Phosphatic fertilisers differ somewhat in their effectiveness according to soil and climate, but correctly used they have a marked effect on the clover content of a sward and subsequently, through enhanced fertility, on the productivity as a whole. Phosphoric acid recovery in the herbage on seriously phosphate-deficient soils is low (E. M. Crowther, *J. Roy. Agric. Soc.* 1934, 95, 34). On Boulder Clay at Cockle Park the recovery from one application was less than 10% over a period of 3 or 4 years during which frequent cuts were taken. The balance of the  $P_2O_5$  is still held in the surface soil. After regular applications of basic slag for 40 years the recovery is higher, and it appears as though a certain degree of soil saturation in regard to phosphoric acid has to be reached before a reasonable recovery of added  $P_2O_5$  is possible in the herbage (J. A. Hanley, *Proc. 4th International Grassland Congress, Aberystwyth*, 1937).

Recent research has shown that the actual returns from the use of fertilisers depend very much on the efficiency of the "management" of the grass, i.e. the methods of utilizing the crop. Methods of cutting and grazing can exert almost as big an influence on the sward as methods of manuring (Martin Jones, *Empire J. Exp. Agric.* 1933, 1, No. 1, 43-45). In fact the condition of large areas of our natural and semi-natural grazings is due entirely to management methods. The influence of extensive sheep grazing, the burning of heather grazings, the use of cattle, the stage at which grass is grazed or cut, and the taking of regular hay crops, all affect botanical composition and quality.

Quality may be affected to such an extent that herbage becomes seriously mineral-deficient. Overseas, in the Dominions and elsewhere, deficiency diseases are common and well recognised (J. B. Orr, "Minerals in Pastures," Lewis, 1929). In this country they are not so pronounced, but there is a good deal of evidence that mineral-deficiency is at least a predisposing cause of certain sheep diseases.

Moreover, the vast changes in methods of stocking grass land, e.g. the increase in the output of milk and of young stock and the slaughter of younger animals for meat, mean that a much bigger proportion of the live-stock carried is either milk-producing or young growing stock removing relatively large amounts of minerals.

The proportion of  $CaO$  in the dry matter of reasonably good grass is usually not less than 1% and of  $P_2O_5$  not less than 0.75%. These percentages are greatly exceeded in many instances. Whilst 0.4%  $P_2O_5$  is a low figure, less than 0.1%  $P_2O_5$  has been observed in the herbage of some open hill grazings (W. L. Stewart and A. Phyllis Ponsford, *J. Comp. Path. and Therap.* 1936, 59, Part I, 49-62).

Generally speaking, the grasses are not as mineral-rich as the clovers or the weeds, but properly managed grass, converted in the young

leafy stage, has a high mineral content (T. W. Fagan and H. T. Watkins, *Welsh J. Agric.* 1932, 8, 144-151). Stapledon has advocated the use of such plants as daisy, plantain and buttercup to some extent on poor upland mineral-deficient grazings.

**INTENSIVE MANURING AND GRAZING.**—The nutritive value of pasture herbage depends very much on the stage of growth at which it is removed. The so-called "intensive management" of grass land is aimed at converting it as nearly as possible at its most nutritious stage of growth, i.e. with the maximum amount of leaf and the minimum of stalk. This stage is usually attained at 4-6 weeks growth from the previous close grazing or cutting. The herbage under normal conditions of growth is then about 6-8 in. high and contains about 20% crude protein in the dry matter. On analysis the dry matter is approximately equivalent to a balanced ration for milk production and can be kept at that stage throughout the season by regularly repeated grazings or cuttings. Such a method makes a heavy drain on plant nutrients in the soil and calls for correspondingly heavy manuring. It also calls for skilful management of the grazing since growth is uneven from month to month in all seasons.

The method involves "rotational grazing" over a series of fields prepared for grazing at intervals, live-stock being concentrated on each field in turn. Theoretically this method is sound but in practice it is interfered with by seasonal changes in rainfall and temperature, so that modifications of the original strict rotational plan are the rule.

The numerous experiments carried out in connection with this method have, however, furnished new and valuable information on the possibilities of grass, and made it clear that as a crop it offers food for live-stock of "production" as well as "maintenance" quality, and further, if it can be preserved at the right stage of growth, material for winter as well as summer "keep."

**GRASS ENSILAGE.**—Although special crops have been grown for ensilage in this country it was not, until feeding stuffs became short during 1914-18, a popular method of preserving grass. If green grass is heaped in a pit or stack, fermentation processes lead to loss of dry matter which in some cases may result in a loss of nutritive value as high as 40%. It is estimated that the average loss is 25%. These processes can be artificially arrested and two methods for doing this have recently been tried:

- (1) Increasing the soluble carbohydrate content by watering on molasses as the heap is made (usually in a silo), and
- (2) Adjusting the  $pH$  by use of hydrochloric or sulphuric acid (A.I.V. process).

The latter method gives the least loss under skilful control but, on the average farm, the method proves difficult to handle and the use of molasses is probably the easier and safer plan (W. M. Davies, G. H. Botham and W. B. Thompson, *J. Agric. Sci.* 1937, 27, 151).

**GRASS DRYING.**—It is, however, possible that artificial drying of young grass of high quality will take its place with other methods of con-

servation. Drying of green fodders, especially lucerne, has been practised for many years, but the drying of young grass was first tried in this country on a really important scale in 1936 when about 10,000 tons of dried grass were produced. In 1937 the process was extended and several new types of drier introduced. It has been established that young grass can be successfully dried without appreciable loss of protein, minerals, carotenoids or digestibility, and the success of the practice depends on:

- (1) The production of an economical drier;
- (2) The regular production of grass of a quality suitable for drying throughout the season; and
- (3) The introduction of this new concentrated food into live-stock rations.

The driers now in use have a rather low output and an improvement of 20% in efficiency would do much to put the cost of dried young grass on a basis comparable with that of other concentrated foods like oil-cakes. Much research remains to be done on the timing of grass which is as dependent on temperature and moisture conditions and on strains of plants used as it is on fertilisers.

Much preliminary work has been done on the nutritive value of young grass (H. E. Woodman and D. B. Norman, *J. Agric. Sci.* 1932, 22, 852-872). With efficient drying young grass loses little of its nutritive value in the process. High temperatures can be used so long as the grass contains sufficient moisture, but the grass is damaged if subjected to high temperatures after it is dry. Usually temperatures of 300-400°C. are used throughout and the grass takes from 10 to 15 minutes to pass through the drier.

Although dried young grass has a high crude protein content, it can scarcely be produced yet at a price to compete with other high-protein feeding stuffs, and the main commercial value depends on its carotene content. Most of the dried grass sold in 1937 was purchased by feeding-stuffs manufacturers and mixed in the form of meal in poultry rations, thus replacing, to some extent, lucerne meal. The carotenoids in dried grass are effective in maintaining colour in the yolk of eggs and in milk during the winter period when green foods are not available. The guaranteed minimum total carotenoid content has, in some cases, been 250 mg. per kg. of dry matter, but dried grass giving nearly 5 times this amount is not unusual.

Young grass after drying is usually stored in fairly air-tight bags as meal, or is tightly baled as it comes from the drier. Exposure rapidly reduces its carotene content.

For information on all aspects of grass drying, see E. J. Roberts, *Agric. Research Council Report*, "Grass Drying," 1937.

**NEW STRAINS OF HERBAGE PLANTS.**—Recent research into the nutritive value of herbage has given added importance to the plant breeder's work. The successful attempts of R. G. Stapledon and his colleagues at the Welsh Plant Breeding Station, Aberystwyth, to breed grasses and clovers of greater persistency in the sward, with high proportion of leaf to stalk, particularly early or particularly late have provided a new and wide

choice of plants for sowing land down to grass to suit modern needs for carefully "timed" production.

#### GRASSES.

Strictly speaking, grasses are meadow and pasture plants belonging to the *Gramineæ*. The term grass, however, is used by the agriculturist to denote the association of plants—grasses, legumes and weeds—found in cultivated swards. The associations vary from soil to soil according to soil reaction (acidity) and general fertility.

Cultivation of grass land usually aims at a sward consisting of perennial ryegrass (*Lolium perenne*) and wild white clover (*Trifolium repens*), the two dominant plants in the best British grazings. Modern seed mixtures for sowing land to grass contain relatively few (4 or 5) species. Strains bred to persist and to produce a high proportion of leaf to stalk are available.

Young leafy grass is very digestible, rich in protein, minerals and carotenoids, and is in general the most reliable and cheapest food for live-stock. Mature grass has a low protein and high fibre content. The clovers and certain weeds (e.g. plantain, daisy, buttercup) are richer in minerals than the grasses.

A. J. H.

"GRAVOCAINE" (v. Vol. I, 369c).

**GREASES.**—The term "grease," originally applied to all kinds of fat having a soft, buttery consistency, is now restricted to low-grade inedible fats (mostly of animal origin) recovered from waste products, such as slaughterhouse and packing-house waste, condemned carcasses, hotel, restaurant and ships' food-wastes, bones, garbage, skins, etc. Lubricating greases, which mostly contain mineral oil products, are not considered in the present article.

In the United States the term "grease" was formerly used to denote inedible hog-fats, as contrasted with "inedible tallow" derived from cattle and sheep; but this differentiation is no longer strictly maintained, especially outside the packing-house, and in general American trade the distinction between "grease" and "tallow" is merely one of consistency, the titer (f.p. of the fatty acids: 37-39.5°C. for greases and 40-45°C. for tallow) serving as a rough guide. Lard and tallow greases, however, can be recovered separately in the large packing establishments, and a distinction is made in the trade between *packers' grease* or *packing-house grease* and other types; the first-named is sometimes accompanied by the statement that it consists wholly of hog fat and is graded in three qualities (of which the first two are further subdivided), viz. "white grease," "yellow grease" and "brown grease." *White grease* resembles lard in appearance and is prepared from cleaned, fresh material which for some reason cannot be put to edible purposes: *yellow grease* comes from condemned or decomposed material, or unwashed carcasses, viscera, etc., whilst *brown grease* represents the lowest grade and is obtained from all kinds of offal, sweepings, catch-basin accumulations, etc.

Outside the packing-house, greases are recovered from hotel and restaurant wastes (*kitchen grease* or *house grease* or *melted stuff*),

condemned carcasses, bones, slaughter-house and butcher's wastes, etc., garbage (see GARBAGE FATS), etc.; all these greases must be looked upon as low-grade varieties or mixtures of lard, tallow, bone fat, horse fat, etc.

They are characterised by a dark colour, a high percentage of free fatty acids and a high content of unsaponifiable matter: they also have an objectionable odour.

The bulk of the greases are obtained either by boiling out the fatty tissues with open steam under pressure in closed digesters (the wet-rendering system; cf. BONE FAT) or by dry-rendering processes in which the comminuted raw material is heated indirectly in jacketed vessels, without the addition of extraneous water, and the liberated grease is recovered by straining and pressing the solid residue (*cracklings*). Any residual grease in the cracklings or in the solid residue (*tankage*) from the wet-rendering process may be recovered by extraction with solvents as *extraction grease*.

The best qualities of grease, notably the packing-house greases, are used as substitutes for lard and tallow in the soap and candle industries. According to L. B. Zapoleon ("Inedible Animal Fats in the United States," Leland-Stanford Univ., Fats and Oils Studies, No. 3, 1929) the bulk of the grease in the U.S.A. is pressed to furnish *grease-(inedible lard-) stearin* and *grease-(lard-) oil*. The latter is used as a lubricant, and in the preparation of cutting and cooling oils for the metal-working trades and soap emulsions for woollen mills, leather finishing, etc. The grease-stearin, like much of the unpressed grease, is employed for the manufacture of soaps, lubricating greases (cup greases), and for the manufacture of red oil (commercial oleic acid, for the preparation of textile soaps, etc.), stearine (for the candle, cosmetic and rubber industries) and glycerin.

A further series of greases arises as by-products of the leather industry: *skin greases* are obtained in the cleaning (scraping) of the skins prior to tanning, whilst various greases may be recovered by extraction from tanned and tawed skins, leather-clippings, wash-leather trimmings, etc.

*Stuffing greases* comprise various mixtures of *dégras* (*q.v.*), horse fat, skin grease, tallow, fish-stearin, egg oil, etc., which are worked into the tanned leather in the stuffing or currying processes. The excess of unabsorbed grease which is scraped off the leather after this treatment is known as *curriers' grease*: if the original stuffing grease consisted of fairly good tallow and whale-stearin, the *hard curriers'-grease* derived from it may be employable in the manufacture of low-class soaps, but if the original stuffing grease contained much unsaponifiable matter, or considerable quantities of fish oils or whale oil, then the proportion of oxidised acids and unsaponifiable matter will be high and render the product useless for soap-making, and such grease will be sold as *animal grease*, or—if the consistency is very soft—as *animal oil*.

*Whale grease* and *fish-stearin*, which represent low-grade stearins or solid glycerides separated from whale oil or fish oils, are chiefly worked up into stuffing greases and *dégras* substitutes.

*Fuller's grease* or *seek oil* is the fatty matter recovered from the soap-suds which have served for scouring silk, woollen or cotton goods by acidifying the waste suds with mineral acid, and consists of a mixture of fatty acids derived from the soap employed, together with any grease present in the goods.

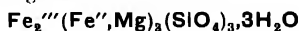
*Wool grease* (wool fat, recovered grease, Yorkshire grease, brown grease; known in the United States as "*dégras*," "English *dégras*" or "German *dégras*") is the crude mixture of wool wax and fatty acids recovered from the soapy liquor used for the scouring of raw wool, by cracking the liquors with mineral acid (cf. black grease, *below*); some wool grease is now recovered by mechanical means, and therefore contains less soapy material or fatty acids. Since the pure wool wax is a wax and not a fat, wool grease differs from the other greases considered in containing no combined glycerin.

Crude wool grease is used as a lubricant (with or without the addition of mineral oils), as a stuffing grease and *dégras* substitute; some is refined for use as "*lanolin*" (pure wool wax) in the preparation of cosmetics, ointments, temporary rust preventives, etc., but the bulk of the crude grease is distilled and worked up in the manner described under black grease (*below*) for the preparation of *distilled grease oleine* (chiefly used as a wool oil) and *distilled grease stearine* (employed as a "sizing tallow" or stuffing grease), and as an inferior material in the soap and candle industries. These products give the *ischolesterol* reaction, and are characterised by the presence of considerable quantities of unsaponifiable hydrocarbon material, produced by decomposition of the neutral wax esters during the distillation.

"*Black grease*" is the dark, almost black, fatty matter which is recovered from cottonseed mucilage (soap-stock) on decomposing this with mineral acid (see COTTONSEED OIL). This black grease is used in the manufacture of low-class candle materials after a purification by distillation with superheated steam and further treatment of the distillate in a manner similar to that practised for the working up of fatty acids in the candle industry.

E. L.

**GREENALITE.** A hydrated iron silicate occurring in the form of green granules in sedimentary rocks, and closely resembling glauconite (*q.v.*), from which it differs in containing no potassium. The composition varies somewhat; one analysis gives the formula



and another



It occurs abundantly on the Mesabi Range in the Lake Superior district of Minnesota, and by its alteration has given rise to ferruginous cherts and immense deposits of iron ore (C. K. Leith, Monograph U.S. Geol. Survey, 1903, 43; F. Jolliffe, Amer. Min. 1935, 20, 405; J. W. Gruner, *ibid.* 1936, 21, 449). A greenalite-chert is found at Glenluce, Wigtonshire (W. Q. Kennedy, Min. Mag. 1936, 24, 433).

L. J. S.

**GREEN-EARTH.** (Ger. *Grünerde*.) A term loosely applied to a variety of earthy minerals of a bluish-green, or dark olive-green colour occurring as alteration products in basic igneous rocks. It includes more particularly the species *celadonite* (or *celadonite*), and various indefinite members of the chlorite group, e.g. *delessite*, *chlorophane*, *kurawite*, *viridite*, etc. Many of these are of indefinite composition and probably mixtures. They are often met with as a green lining in the amygdaloidal cavities of altered basaltic rocks, and form the "skin" of agates and other secondary minerals filling these cavities. Crystals of *augite* in the same rocks are sometimes completely altered to a soft aggregate of green-earth still preserving the sharp outlines of the original crystals. Similar pseudomorphs after *hornblende* also occur. Larger irregular masses fill cavities and fissures in these rocks. The well-known green-earth of Monte Baldo near Verona is referable to *celadonite* (K. Hummel, Chem. Erde, 1931, 6, 468). An analysis of material from this locality gave:  $\text{SiO}_2$  54.84,  $\text{TiO}_2$  0.10,  $\text{Al}_2\text{O}_3$  1.22,  $\text{Fe}_2\text{O}_3$  19.16,  $\text{FeO}$  4.39,  $\text{MnO}$  0.28,  $\text{MgO}$  5.34,  $\text{CaO}$  0.24,  $\text{Na}_2\text{O}$  0.82,  $\text{K}_2\text{O}$  9.75,  $\text{H}_2\text{O}$  3.77, total 99.91 (Gumbel, 1896). This composition is very similar to that of *glauconite*, with which *celadonite* is perhaps identical, differing only in its state of aggregation and mode of origin and occurrence. This *celadonite* green-earth is worked commercially as a pigment in the Italian Tyrol; and similar material could be obtained from many other localities.

**GREEN EBONY.** This yellow dyewood, a native of Jamaica or West Indies, is obtained from the *Excoecaria glandulosa* Siv. or *Jacaranda ovalifolia* R. B. The trunk of the tree is about 6 in. in diameter; the wood is very hard and of an orange-brown colour when freshly cut, and stains the hands yellow. Bancroft, "Philosophy of Permanent Colours," 1813, ii, 106, and O'Neill, "Dictionary of Calico Printing and Dyeing," 1862, mention the use of this dyewood in dyeing greens and other compound shades, sometimes in place of old fustic, but it does not appear at any time to have been largely employed. It was also used to some extent as a dye for leather and for greenish blacks in silk dyeing.

Perkin and Briggs (J.C.S. 1902, 81, 210) examined green ebony and isolated two crystalline colouring matters, *excoecarin* and *jacarandin*; these were distinguished by the fact that only the latter is precipitated by lead acetate. About 17 g. *excoecarin* and 3 g. *jacarandin* were obtained from 8 kg. of the wood.

*Excoecarin*,  $\text{C}_{13}\text{H}_{12}\text{O}_5$ , lemon-yellow needles, melts with effervescence at 219–221°, and is soluble in aqueous and alcoholic alkaline solutions, forming violet-red liquids which are rapidly oxidised on exposure to air and assume a brown tint.

The *tribenzoyl* derivative forms colourless needles, m.p. 168–171°, and the *dimethyl ether* yellow needles, m.p. 117–119°. On fusion with alkali, *excoecarin* gives hydroquinone carboxylic acid (2,5-dihydroxybenzoic acid) and a substance melting at 124° which is probably hydro-toluquinone (2,5-dihydroxytoluene).

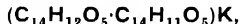
By the action of bromine, *excoecarin* is oxidised to *excoecarone*,  $\text{C}_{13}\text{H}_{10}\text{O}_5$ , flat copper-coloured needles or leaflets, m.p. about 260°, and this is reconverted into *excoecarin* by the action of sulphurous acid. With an alcoholic solution of quinine, *excoecarin* gives the compound  $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{C}_{13}\text{H}_{12}\text{O}_5$ , minute green leaflets, m.p. 190° (decomp.), from which sulphurous acid also regenerates *excoecarin*. Since the latter contains a quinol or toluquinol nucleus, *excoecarone* is thus probably a *p*-quinone (Perkin, *ibid.* 1913, 103, 657).

*Excoecarin* does not dye mordanted fabrics, but is a substantive dyestuff in that it has a weak but decided affinity for the animal fibres with which it gives, preferably in the presence of tartaric or oxalic acid, yellow shades.

*Jacarandin*,  $\text{C}_{14}\text{H}_{12}\text{O}_5$ , yellow plates or leaflets, m.p. 243–245°, dissolves sparingly in alcohol and the usual solvents to form pale yellow liquids having a green fluorescence. With alkali hydroxides it gives orange-red solutions, with alcoholic lead acetate a bright orange precipitate, and with alcoholic ferric chloride a dark greenish-black solution. It dyes mordanted woollen fabrics the following shades:

Chromium	Aluminium	Tin.	Iron.
Dull yellow-brown.	Orange-brown.	Bright golden yellow.	Deep olive.

*Diacetyljacarandin*, pale yellow needles, m.p. 192–194°, when digested with boiling alcoholic potassium acetate, yields the salt



yellow needles. *Dibenzoyljacarandin*, yellow prismatic needles, melts at 167–169°.

As indicated by Bancroft (*op. cit.*), the colours given by green ebony are similar in character to those yielded by old fustic. Employing mordanted woollen cloth, the following shades are produced:

Chromium	Aluminium	Tin.	Copper	Iron
Dull yellow-brown.	Dull brown-yellow.	Golden yellow.	Pale brown.	Olive-green.

A. G. P. and E. J. C.  
**GREENOCKITE.** Cadmium sulphide,  $\text{CdS}$ , crystallised in the hexagonal system with hemimorphic development and isomorphous with *wurtzite* ( $\text{ZnS}$ ). This and the still rarer cadmium oxide, and *otavite* (basic carbonate), are the only minerals that contain cadmium as an essential constituent. Distinct, though small, crystals have been found in Scotland, in the neighbourhood of Glasgow. They occur very sparingly with *piechite* in amygdaloidal basalt in the Bishopton railway-tunnel, in the Boyleston quarry at Barrhead in Renfrewshire, and in the Bowling quarry in Dumbartonshire. They are honey- to orange-yellow, transparent to translucent, and have a resinous to adamantine lustre; the streak is orange to reddish-yellow. Sp.gr. 4.8–4.9; hardness 3–3½. Minute (0.05 mm.) red crystals have been found at Llallagua, Bolivia (S. G. Gordon, Not. Nat. Acad. Nat. Sci. Philadelphia, 1939, No. 1). Traces of cadmium are often present in zinc-blende (up

to 1.5%, and in the ores of the Joplin district in Missouri averaging 0.358%, and with the weathering of this mineral cadmium sulphide remains as a thin, powdery, canary-yellow coating ("cadmium-ochre"), or it may impart a tinge of colour to the secondary zinc minerals *hemimorphite* and *smithsonite* ("turkey-fat ore"). In this form the mineral is known from many localities, though never in large amount. Being colloidal, it does not agree with the definition of greenockite as given above; and, again, the possible existence of a cubic form of cadmium sulphide is suggested by the isomorphous presence of this constituent in zinc-blende, although this modification has not been prepared artificially. The name *xanthochroite* (A. F. Rogers, 1917) has therefore been suggested for this colloidal form of cadmium sulphide. Hemimorphic hexagonal crystals of cadmium sulphide have been prepared artificially, and they are not uncommon as furnace products. The artificial crystals have sp.gr. 4.820 and the high refractive indices  $\epsilon_{Na}$  2.529,  $\omega_{Na}$  2.506.

L. J. S.

GREEN STONE (v. Vol. IV, 8a, 53b).

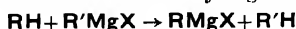
GRÈGE (v. Vol. V, 94a).

GRISHEIM CELL (v. Vol. III, 50d).

**GRIGNARD REAGENTS.** Unsymmetrical magnesium compounds of type  $RMgX$  where  $R$  = an organic residue and  $X$  = halogen. The use of Grignard reagents in organic chemistry may be traced to the use by Barbier (Compt. rend. 1898, 128, 110) of magnesium in place of zinc when condensing methyl iodide with methylheptenone. After unsuccessful attempts to exploit this innovation Grignard (Ann. Chim. Phys. 1901, [vii], 24, 437), believing that the more electropositive magnesium should be more reactive than zinc, showed that alkyl iodides react at room temperature with magnesium, and since then such reagents have been widely used for synthetic purposes. They do not normally exist in the free form  $RMgX$  but are combined with one (Blaise, Compt. rend. 1901, 132, 839; Grignard, *ibid.* 1901, 132, 558) or two (Tschelinceff, Ber. 1904, 37, 2084, 4534; 1905, 38, 3664; 1906, 39, 773) molecules of ether; the latter may be replaced by tertiary amines, sulphones or organic compounds of selenium, tellurium or phosphorus. These secondary reactants are only catalysts and, using minor quantities of these, Grignard reagents may be obtained in the solid state from benzene solution. When isolated they are inflammable in air but fortunately may, with few exceptions, be used in ether or other solution without isolation.

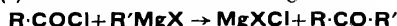
For synthetic purposes the reactions of Grignard reagents may be summarised as follows:

(a) Reaction with active hydrogen atoms



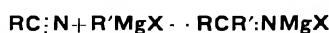
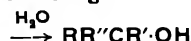
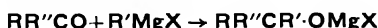
When  $R'$  is a lower aliphatic group 1 mol. of gaseous paraffin is liberated for each carboxyl, hydroxyl or  $NH$ -group present; this reaction provides the basis of the Tschugaeff-Zerewitinoff determination of such groups (Pregl-Roth, "Die quantitative organische Mikroanalyse," 1935) and further reactions of the  $N$ -magnesium compounds afford valuable routes to  $C$ -homologues in the pyrrole, indole and other series.

(b) Reaction with reactive halogen atoms



When excess of the reagent is used the resulting ketone may react further to give a tertiary alcohol.

(c) Most of the synthetic applications depend on the addition of Grignard reagents to unsaturated groupings:



Clearly when two such groups are present in the same molecule reaction becomes more complex although the entering Grignard reagent usually shows a preference for one of the centres of possible reaction.

*Reviews.*—Schmidt, Ahrens Sammlung, 1906, 10, 67, 146; 1908, 13, 357, 446; Hepworth, J.S.C.I. 1922, 41, 7; Courtot, "Traité de Chim. Org.", 1937, V, 86; the last is unusually complete and contains an exhaustive bibliography.

GRISEOFULVIN (v. Vol. V, 58c).

GRI-SHI-BU-ICHI. Japanese name for an alloy of copper and silver of a rich grey colour.

GRISON TETRYLITE COUCHE (v. Vol. IV, 487b).

GRISOU NAPHTHALITE-ROCHE (v. Vol. IV, 474d).

GRISOUTINE COUCHE (v. Vol. IV, 553b).

GRISOUTINE ROCHE (v. Vol. IV, 553b).

GROG (v. Vol. V, 566a).

**GROTTTHUS-DRAPER LAW.** Photochemical reaction can only be brought about by radiation which is absorbed by some component or components of the system in which the reaction occurs. Stated in these broad terms this may be taken as the fundamental postulate of photochemistry. Its first expression we owe to Grotthus (Ostwald's Klassiker, 1817, No. 152, p. 101) who deduced that only light which is absorbed by a substance can cause it to become chemically active. Grotthus' paper was, however, rather rapidly forgotten and his proposition was independently restated by Draper (Phil. Mag. 1841, [iii], 19, 195), who was also able to provide, in a series of later papers, an experimental verification of the law as a result of his studies of the photochemical union of hydrogen and chlorine. The law is accordingly associated with the names of both workers.

While the law is without exception, it is entirely qualitative, the nature of the reactivity, the spectral region which is effective (for the law's converse that all light which is absorbed produces chemical change is far from true), and the relation between the amount of chemical reaction and the energy absorbed, are all undefined and must be determined by experiment. Neither is it necessary that the absorbing substance be a reactant, as exemplified by the important phenomenon of photo-sensitisation, in which the light is absorbed by a molecule (e.g. mercury) which, after transferring the energy it has

absorbed to a reactant molecule, takes no part in the subsequent chemical change.

Quantitative expression of the relation between the energy absorbed and the amount of chemical reaction, and, indeed, any coherent study of photochemistry, had to await the development of the quantum theory and of the theory of chain reactions.

D. W. G. S.

**GROUND NUT.** A term often used to describe the tuberous roots of the earth nut (*Dunium* spp.) or the peanut (*Arachis hypogaea*). According to Wynton the term is more properly restricted to the dark brown root swellings of *Apios tuberosa*. These "tubers," which are of similar size and shape to a hen's egg, grow wild in many parts of America and are cultivated in central European countries as a substitute for potatoes.

Typical analyses of the American ground nut and of a Japanese variety (*A. fortunei*) are:

	I	II.
Water . . .	70.7	68.6
Crude protein . . .	4.06	4.19
True protein . . .	1.88	1.56
Fat . . .	1.00	0.19
N-free extract . . .	18.65	24.54
Starch . . .	7.02	18.30
Pentosans . . .	2.60	1.46
Fibre . . .	3.55	1.20
Ash . . .	2.05	1.30

I. *A. tuberosa* (Brigghetti, Staz. sper. agr. Ital. 1000, 33, 72)

II. *A. fortunei* (Hemmi, J. Coll. Agric. Hokkaido, 1918, 8, 33)

According to Hemmi the carbohydrates of *A. fortunei* include reducing sugars 1.15, non-reducing sugars 2.85, dextrin 1.0 and galactan 1.02%. The hemicellulose of *A. tuberosa* yields L-arabinose and D-galactose on hydrolysis.

A. G. Po.

**GROWAN** (v. Vol. III, 32c).

**GROWTH - PROMOTING SUBSTANCES** are substances which have the power of regulating the form and rate of growth in the plant world (see AUXIN). They are sometimes referred to as "plant hormones," but the term is in many respects inappropriate. There is no evidence that growth-promoting substances are secretions of special organs as is the case with animal hormones. The association of high concentrations of auxin with rapid vegetative growth in the aerial parts of plants has already been referred to (AUXIN). The opposite direction of growth with heteroauxin (indole-3-acetic acid) in stimulating root formation has now found its obvious horticultural application and commercial preparations of this and related substances are now marketed for inducing the rapid rooting of plant cuttings. Tinker (J. Roy. Hort. Soc. 1936, 61, 510; 1938, 63, 210; 1939, 64, 554) records the results of rooting trials with a large number of plant species, using a variety of pure and commercial samples of growth-promoting substances.

From time to time additions are made to the number of substances exhibiting growth-regulating ability and in some cases, e.g. that

of naphthylacetic acid, activity exceeding that of the naturally-occurring heteroauxin is recorded (Pfahler, Jahrb. wiss. Bot. 1938, 86, 675). According to Koepfli, Thimann and Went (J. Biol. Chem. 1938, 122, 763), growth-promoting activity is dependent on a particular molecular structure which includes the following characteristics: (i) a nuclear ring system containing a double bond; (ii) a side-chain containing a carboxyl group (or a group from which this is easily derived) separated from the nucleus by at least one C atom; (iii) a particular space relationship between the side-chain and the nucleus. Other investigations by Thimann *et al.* suggest that the effect of growth-promoting substances within the plant is initiated by its action in increasing protoplasmic streaming, this being influenced by respiratory activity (oxygen supply) and by the concentration of growth-promoting substance present. It would appear that heteroauxin acts upon the cell substance rather than on the cell wall. Went (Plant Physiol. 1938, 13, 55) advances the theory that in the higher plants growth-substances do not alone produce their characteristic effects on growth, but operate by controlling the distribution within the plant of other substances, described as "calines." *Caulocaline*, *rhizocaline* and *phyllocaline* are natural plant constituents essential for the elongation of stems and lateral buds, for root formation and for leaf growth respectively.

The action of heteroauxin on plant growth is enhanced by the presence of accessory substances, e.g. certain amino-acids, notably proline, and by vitamin B<sub>1</sub> (aneurin), a minimal amount of which is probably essential for the action of the growth-promoting substances.

The sealing of plant wounds is brought about by the rapid production of new tissue by division of adjacent cells. English and Bonner (J. Biol. Chem. 1937, 121, 791) ascribe this sudden stimulation of cell activity to the action of a growth-promoting substance (wound "hormone") which they name *traumatin*, the isolated methyl ester of which has the formula C<sub>11</sub>H<sub>17</sub>O<sub>4</sub>N. A later paper by English, Bonner and Haagen-Smit (Proc. Nat. Acad. Sci. 1939, 25, 323) reports the isolation of a second wound "hormone," a dibasic acid of formula C<sub>12</sub>H<sub>20</sub>O<sub>4</sub>.

*Bios*, the growth-promoting substance associated with yeast growth for a number of years, is now regarded as containing at least five constituent factors:

(a) *meso*-Inositol, a necessary growth factor for nearly all types of yeasts.

(b) *Pantothenic acid*, a complex of  $\beta$ -alanine with an unidentified hydroxy-acid, to the calcium salt of which Williams *et al.* (J. Amer. Chem. Soc. 1939, 61, 464) assign the formula (C<sub>8</sub>H<sub>14</sub>O<sub>7</sub>N)<sub>2</sub>Ca. Pantothenic acid is also of considerable importance in the animal world, in which it is actively concerned in carbohydrate metabolism, and occurs in considerable amounts in the liver and muscles. Jukes (*ibid.* 1939, 61, 975) records the close similarity between pantothenic acid and the chick anti-dermatitis factor.

(c) *Aneurin* [v. Vitamin B<sub>1</sub>] accelerates the fermentation activity of a number of yeasts, the pyrimidine rather than the thiazole com-



ponent of the vitamin being associated with its activity.

(d) Vitamin  $B_6$  has also been shown (Schulz *et al.*, *ibid.* 1939, **61**, 1931) to stimulate fermentation activity and the reproduction in yeast.

(e) *Biotin*, isolated by Kögl, is a widely distributed and essential growth factor for yeasts (Chem. and Ind. 1938, **57**, 49).

Aneurin is also of importance in the growth of a number of moulds. In this case also the physiological activity appears to be associated with the pyrimidine constituent, although the thiazole component must also be present. In some cases organisms grow satisfactorily if either the vitamin or the thiazole component is added to the nutrient medium but not if the pyrimidine constituent alone is given. In such cases it is presumed that the organism can synthesise the pyrimidine but not the thiazole portion of the vitamin molecule. Other organisms appear to be able to synthesise the whole vitamin and others must be supplied externally with the vitamin or its constituent pyrimidine and thiazole derivatives. A possible scheme of classification of the lower organisms on the basis of their requirements in respect of aneurin, or its pyrimidine or thiazole components, or of a mixture of these is indicated by Robbins (Proc. Nat. Acad. Sci. 1938, **24**, 53).

Nicotinic acid and nicotinamide may also serve as growth factors for certain bacteria (Knight and McIlwain, Biochem. J. 1938, **32**, 1241) and are possible constituents of the bios complex.

A. G. Po.

**GUAIACETIN.** Sodium salt of the *o*-hydroxyphenyl ether of glycollic acid.

**GUAIACOL** (*Monomethorycatechol*),



is a distillation product of guaiacum resin (Herzig and Schiff, Monatsh. 1898, **19**, 95), and occurs in beechwood tar, from which it can be separated by treating the fraction of the tar that comes over at 200–205° with ammonia to remove acids; it is then again fractionated, and the lower boiling fraction is dissolved in ether and treated with potassium hydroxide. The potassium salt of guaiacol is filtered, washed with ether and recrystallised from alcohol, after which it is decomposed with sulphuric acid, and the guaiacol redistilled. (For other methods of separation, *cf.* G.P. 87971, 56003, 100418; Chem. Zentr. 1899, **1**, 764.) Guaiacol is prepared from *o*-anisidine. 500 g. *o*-anisidine are diazotised, and the solution of the diazo salt is then poured into a boiling solution of 600 g. of copper sulphate in 600 c.c. of water. The guaiacol is then separated by distillation in steam (G.P. 167211; Frdl. 1905–7, 128; *cf. also* G.P. 95339; J.S.C.I. 1898, **17**, 269, 314).

Pure guaiacol can be obtained by dissolving catechol (55 parts) in ethyl alcohol (2,000 parts) and adding nitrosomonomethyl urea. The mixture is cooled to 0° and 20 parts of sodium hydroxide dissolved in a small quantity of water are added, drop by drop, with constant stirring. The solution is filtered, the alcohol distilled off, and the residue is fractionated *in vacuo* (G.P. 189843; Frdl. 1905–7, 1161).

Guaiacol is also prepared by heating an equimolecular mixture of catechol, potash and potassium methylsulphate under pressure at 170–180°, or by heating catechol and methyl iodide in methyl alcohol. In another method a weak base, such as sodium hydrogen carbonate, is gradually added to a mixture of catechol with the alkali or alkaline earth salts of methylsulphuric acid, in the presence of veratrole as diluent at 160–180° (Zollinger and Rohling, G.P. 305281; J.C.S. 1918, **114**, i, 497). Thompson (B.P. 5284, 1893) suggests the purification of guaiacol by treatment with a freezing mixture.

Guaiacol made by the ordinary commercial methods is impure; it is hygroscopic and has a low m.p. Moser and Ver. f. Chem. Ind. A.-G. (U.S.P. 1651617 (1927); G.P. 484539 (1925)) have described an improved process. If an insufficient amount of alkali is added to the tar oils the monomethyl ethers of dihydric phenols are first dissolved, and this selective action enables them to be separated from the non-methylated phenols. (For synthetic methods, *see* Bergstrom and Cederquist, Iva, 1931, **1**, 14; Jakubowski, Roczniki Farm. 1933, **11**, 1; Sumarokov, Lesokhimiicheskaya Prom. 1933, No. 3, **2**, 34; Bentley and Catlow, U.S.P. 1980901; Dominikiewicz, Arch. Chem. Pharm. 1934, **1**, 1; Gubelmann, Welland and Stallmann, U.S.P. 1623949 (1927); Titherley and Hudson, U.S.P. 1878061 (1932); I.G. Farbenind., A.-G., Marx and Lehmann, G.P. 591534).

Guaiacol has a characteristic odour and crystallises in long vitreous transparent prisms, which appear rose-red in sunlight; m.p. 28.5°, b.p. 202.4°/738 mm. (Freys, Chem.-Ztg. 1894, **18**, 565); sp. gr. 1.140 at 25°. When quite pure it is non-caustic and non-poisonous (Béhal and Choay, Compt. rend. 1893, **118**, 197; Kuprianow, J.S.C.I. 1895, **14**, 57). Dilling, "Materia Medica," 1939, 394, states that it is less toxic than phenol.

It is soluble in most organic solvents, and to a less extent in water. The solubility of guaiacol in glycerol is given by J. A. Roborgh, Dissertation, Amsterdam (1927): 9.05 g. of guaiacol is dissolved by 100 g. glycerol (98.2%, Dutch and German Pharmacopœias) at 20°; the figure in French and British Pharmacopœias (sp.gr. 1.2612, 86.5%) is 13.1 at 20°. With a trace of ferric chloride its alcoholic solution gives a blue colour, which becomes emerald-green on the addition of more ferric chloride.

Guaiacol is employed in pharmacy as an expectorant and intestinal antiseptic; also in pulmonary tuberculosis, in cases of typhoid and other fevers, and for the relief of superficial neuralgia. For esters of guaiacol possessing therapeutic properties, *see* B.P. 316750 (1928); 317194 (1928).

**Tests.**—(1) 2 c.c. of guaiacol mixed with 4 c.c. of light petroleum should separate at once into 2 layers. (2) 1 c.c. of guaiacol should dissolve in 2 c.c. of *N*-sodium hydroxide when heated; on cooling the mixture should congeal to a white saline mass, which gives a clear solution with 20 c.c. of water. (3) 1 c.c. of guaiacol shaken with 10 c.c. of sulphuric acid should give a pure yellow colour (British Pharmacopœia, 1932). For other tests, *see*

Marfori, J.S.C.I. 1891, **10**, 487; Fonzes Diacon, Bull. Soc. chim. 1898, [iii], **19**, 191; Guérin, J. Pharm. Chim. 1903, [vi], **17**, 173.

A solution of  $\text{SbCl}_5$  in chloroform gives a light brown coloration (or olive-brown), changing to deep green, blue-green and finally deep blue. Guaiacol carbonate gives a lemon or sulphur yellow (Ekkert, Pharm. Zentrallhalle, 1934, **75**, 49).

Guaiacol (0.05 g.) is dissolved in 5-10 c.c. conc.  $\text{HCl}$ , a minute crystal of sodium nitrite added and the mixture very gradually heated nearly to boiling, then cooled or diluted and poured into excess of 10% ammonia. Guaiacol gives a green colour. (In the acid stage guaiacol and other phenols often give a red colour.) (Ware, Analyst, 1927, **52**, 1927.)

A micro test for guaiacol is the characteristic precipitate given by diazo-*p*-nitraniline (Rosen-thaler, Mikrochemie, 1935, **19**, 17).

Wischo describes colour tests for guaiacol with  $\text{FeCl}_3$ , Jorisson's reagent, aqueous ammonium vanadate, and  $\text{V}_2\text{O}_5$  in dilute  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ , and oxalic acid, respectively (Pharm. Monatshefte, 1928, **9**, 169).

For the estimation of guaiacol by a colorimetric method, 0.5 g. of the sample is dissolved in a little water, 10 c.c. of alcohol added, and the solution made up to 1,000 c.c.; 20 c.c. of this solution are mixed in a test-tube with 1 c.c. of sodium nitrite solution (1:100) and 1 c.c. dilute nitric acid (1:200). A characteristic red-brown colour is produced, which is compared within about 10 minutes with the colorations given by suitable standard solutions (Adrian, Z. anal. Chem. 1901, **40**, 624). For the estimation of guaiacol in pharmaceutical preparations, see Dominkiewicz, Chem. Zentr. 1931, **11**, 284; Chernoff, J. Amer. Chem. Soc. 1929, **51**, 3072; Christie and Menzies, J.C.S. 1925, **127**, 2369.

Guaiacol (or its carbonate) may be estimated gravimetrically as the derivative precipitated by the action of iodine in  $\text{KI}$  (cf. aristol from thymol; François and Seguin, Bull. Soc. chim. 1933, [iv], **53**, 711). See also Knight, J. Assoc. Off. Agric. Chem. 1931, **14**, 367, and Meldrum and Patel, J. Indian Chem. Soc. 1925, **5**, 91.

For estimation of guaiacol in urine, see Schmid, Z. physiol. Chem. 1932, **205**, 213.

Guaiacol, when treated with hydrogen cyanide, in the presence of sodium or zinc chloride, yields vanillin (Roesler, G.P. 189037; Frdl. 1905-7, 1280; Guyot and Gry, Compt. rend. 1909, **149**, 028; Bull. Soc. chim. 1910, [iv], **7**, 902). Barium guaiacolate is insoluble in neutral solvents, 100 parts of water dissolve 4.4 parts at 20°; it is partly hydrolysed by hot water. The calcium salt has similar properties (Sumarokov, Lesokhimicheskaya Prom. 1933, No. 3, 2, 34). Copper salt, see Nakatsuka and Inuma, Bull. Chem. Soc. Japan, 1936, **11**, 358.

Guaiacolonosulphonic acids can be obtained by treating guaiacol with sulphuric acid between 0° and 140°. The mixture of 2-methoxyphenol-5-sulphonate (m.p. 106-108°), and 2-methoxyphenol-4-sulphonate (m.p. 97-98°) is separated by converting them into the basic salts of the alkaline earths, or of the heavy metals, the salts of the former acid being readily soluble in water, whereas those of the latter are insoluble or

sparingly soluble. By the action of hydrogen sulphide, or some suitable acid, the salts are then converted into their respective acids (G.P. 188506; Frdl. 1905-7, 936; G.P. 132607; Frdl. 1900-02, 113; G.P. 212389; Hähle, J. pr. Chem. 1902, [ii], **65**, 95; Lamière and Perrin, Bull. Soc. chim. 1903, [iii], **29**, 1228; Rising, Ber. 1906, **39**, 3685; Paul, *ibid.* [vii], **73**, 4093; André, J. Pharm. Chim. 1898, [273], **7**, 324). With nitric acid the latter acid forms yellow dinitroguaiacol (m.p. 122°), whilst the former acid merely gives a dark red coloration. It is important that when the former acid is used therapeutically, it should be free from the latter compound which gives rise to secondary reactions (Ellis, J.S.C.I. 1906, **25**, 335).

The alkali guaiacolsulphonates are employed as drugs (Alpers, U.S.P. 692588; J.S.C.I. 1902, **21**, 364). Tagliavini has prepared salts of the sulphonates with antipyretic and analgesic bases (Boll. Chim. farm. 1909, **48**, 6).

Carbonyl chloride condenses with the alkali guaiacolsulphonates in alkaline solutions, giving derivatives such as potassium carbonatodiguaiacol-disulphonate  $\text{CO}[\text{OC}_6\text{H}_3(\text{OMe})\text{SO}_3\text{K}]_2$ , and potassium carbonatodiguaiacolsulphonate,



(Einhorn, G.P. 203754, 1909).

A number of compounds of *o*-guaiacolsulphonic acid with alkaloids are described by Schaefer (J.S.C.I. 1910, **29**, 928).

*Guaiacyl benzoate* ("Benzosol," benzoyl guaiacol),  $\text{C}_6\text{H}_5\text{CO}\cdot\text{OC}_6\text{H}_4\text{OMe}$ , is a colourless, odourless, tasteless powder, almost insoluble in water, readily soluble in organic solvents. It has m.p. 56°, and is used in the treatment of pulmonary tuberculosis (B.P. 5366, 1890; J.S.C.I. 1891, **10**, 383; Walzer, Chem.-Ztg. Rep. 1891, **15**, 165).

*Guaiacyl cinnamate* ("Styracol," cinnamyl guaiacol),  $\text{C}_6\text{H}_7\text{CO}\cdot\text{OC}_6\text{H}_4\text{OMe}$ , from guaiacol and cinnamoyl chloride. It forms colourless needle-shaped crystals, m.p. 130°, which are employed in catarrhal affections of the digestive tracts, and in the treatment of phthisis.

*Guaiacyl valerate*,  $\text{C}_4\text{H}_9\text{CO}\cdot\text{OC}_6\text{H}_4\text{OMe}$ , a yellowish oily liquid, b.p. 245-265°, is used in medicine under the name of *Geosol* (Rieck, J.S.C.I. 1897, **16**, 632).

*Guaiacyl salicylate* (guaiacol-salol),



is a white crystalline, odourless, tasteless powder; m.p. 65°.

*Guaiacyl succinate*,  $\text{C}_2\text{H}_4(\text{CO}\cdot\text{OC}_6\text{H}_4\text{OMe})_2$ , fine silky needles; m.p. 136°.

"*Guaiamar*," the glyceryl ether of guaiacol,  $\text{C}_6\text{H}_4(\text{OMe})\text{OC}_3\text{H}_7\text{O}_2$ , is formed by the action of anhydrous glycerol on guaiacol. It is a white crystalline body, m.p. 75°, soluble in water and in most organic solvents. It was suggested as an antiseptic for internal and external application (J.S.C.I. 1900, **19**, 371; 1902, **21**, 1346).

*Guaiasanol* (guaiacyl diethylaminoacetate hydrochloride),  $\text{MeO}\cdot\text{C}_6\text{H}_4\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{NEt}_2\cdot\text{HCl}$ , m.p. 184° (Einhorn, Chem.-Ztg. Rep. 1900, **24**, 33; J.S.C.I. 1900, 464). By the action of the monochloroacetic esters of phenols with secondary

amines of the fatty series, many compounds, similar to the above, have been prepared (Einhorn and Hütz, Arch. Pharm. 1902, **240**, 631; G.P. 105346). They are non-poisonous, odourless and strongly antiseptic substances.

*Guaiacyl ethoxyacetate*,



is a colourless, odourless oil, b.p. 150°/10 mm. The corresponding methoxy derivative boils at 170–171°/10 mm., and has very similar properties to the ethoxy derivative. Both substances are non-poisonous, and can be used therapeutically as external remedies (G.P. 171790; Frdl. 1905–07, 933).

*Guaiacum (Geoform)* is produced by the condensation of guaiacol (2 mol.) with formaldehyde (1 mol.). It is a tasteless, yellow, non-irritant and non-toxic powder (Ehlert, Pharm. J. 1902, **68**, 61). Guaiacol condenses with formaldehyde and  $(\text{CH}_3)_3\text{NH}$  to form 2-hydroxy-3-methoxybenzyl dimethylamine, m.p. 46–47°, b.p. 127–129°, soluble in alkali (Décombe, Compt. rend. 1933, **197**, 258).

*(Guaiacyl carbonate ("Duotal"))*,

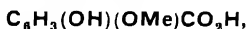


is prepared by passing phosgene into a solution of guaiacol in sodium hydroxide. It is a white crystalline powder, m.p. 85–88°, soluble in most organic solvents, but insoluble in water. Its alcoholic solution yields no characteristic colour with ferric chloride. Therapeutically it is very similar to guaiacol (G.P. 99057, 58129, 117346, of 1898; G.P. 224160; Einhorn, Chem. Zentr. 1910, II, 518; see also Mazover, Russ.P. 35192 (1934); Ekkert, Pharm. Zentralh. 1932, **73**, 504).

*Guaiacyl thymyl carbonate*, b.p. 222–225°/15 mm. is an emulsifying agent, also a solvent for dyes and lacquers (Hurwitz, Swiss P. 180050, 1936).

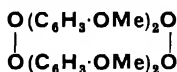
*Guaiacyl chlorocarbonate* is a colourless oil b.p. 112°/25 mm. It is prepared by the interaction of antipyrine, carbonyl chloride and guaiacol (G.P. 117624 of 1899; Einhorn, G.P. 224108, 1908; Chem. Zentr. 1910, II, 517).

*Guaiacol carboxylic acid*,



is formed by the action of carbon dioxide on the previously heated sodium derivative of guaiacol; the free acid crystallises from water or dilute alcohol as a white, odourless crystalline powder, m.p. 148–150°. Its aqueous solution is coloured blue by ferric chloride. The acid and its salts have been recommended as antiseptics and anti-rheumatics (Pharm. J. 1890, 977).

*Tetraguaiacquinone*, formed when guaiacol is oxidised with laccase,



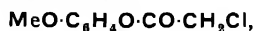
is a fine crystalline powder, m.p. 135–140°, having a purplish-red colour with a faint green metallic lustre. It is insoluble in water, but gives mahogany-red solutions with chloroform and with acetic acid. It also forms coloured solu-

tions in alkalis (Bertrand, Compt. rend. 1903, **37**, 1269).

*Hexamethylenetetraminetriguaiacol* crystallises as brilliant needles, which become soft at 80° and melt to a turbid liquid at about 95°. When distilled in steam it yields guaiacol (B.P. 24072, 1908; J.S.C.I. 1909, **28**, 490).

*Guaiacyl acetate*, b.p. 123–124°/13 mm., readily undergoes intramolecular rearrangement, on which a new synthesis of vanillin has been based (Mottorn, J. Amer. Chem. Soc. 1934, **56**, 2108).

*Guaiacyl chloro-acetate*,



is prepared by treating a mixture of guaiacol, monochloroacetic acid and pyridine with phosphorus oxychloride. It forms white needles, m.p. 58–60° (Einhorn and Hutz, l.c.).

*Guaiacol picrate* forms orange-red needles; m.p. 88–89°.

*Benzyl guaiacol* is a yellow, beautifully fluorescent oil; b.p. 269–270°/436 mm. (Boscogrande, Chem. Zentr. 1898, I, 207).

Many other guaiacol derivatives have been prepared, some of which have been recommended for use in medicine (B.P. 5856, 1894; Ruhemann, J.C.S. 1902, **81**, 421; G.P. 120558; Frdl. 1900–02, 1112; G.P. 157355; Frdl. 1902–04, 616; Knapp and Suter, Chem. Zentr. 1904, I, 391; Moureu and Lazenne, Compt. rend. 1906, **142**, 894; Bischoff, Ber. 1906, **39**, 3846; Gattermann, Annalen, 1907, **357**, 313; Fournneau, J. Pharm. Chim. 1910, [vi], 1, 55, 97; Manchot, Ber. 1910, **43**, 949; Wohl and Bertold, *ibid.* 2175; Hoffmann, G.P. 255924; Chem. Zentr. 1910, II, 1105).

A number of azo-derivatives of guaiacol are described by Leonardi (Atti R. Accad. Lincei. 1907, [v], **16**, ii, 630); some nitro- and amino-derivatives by Reverdin and Crépieux, Ber. 1903, **36**, 2257; 1906, **39**, 4232; Paul, *ibid.* 2773; Kuhlmg, *ibid.* 1905, **38**, 3007; Fichter and Schwab, *ibid.* 1906, **39**, 3339; Pollecoff and Robinson, J.C.S. 1918, **113**, 645.

*Thioguaiacol* and *thioguaiacyl xanthate* have been prepared by Mauthner (Ber. 1906, **39**, 1347).

Guaiacol forms mono-, di-, tri- and tetra-halogen derivatives (Cousin, Compt. rend. 1898, **127**, 759; Tassily and Leroide, *ibid.* 1907, **144**, 757; Bull. Soc. chim. 1908, [iv], **3**, 124; Mameli, Gazzetta, 1907, **37**, ii, 366; Robertson, J.C.S. 1908, **93**, 791). The iodo-derivatives are said to be applicable in medicine (Mameli and Pinna, Chem. Zentr. 1907, II, 2044).

*Guaiacyl phosphite*, m.p. 75–5°, is a white crystalline powder, with a piquant non-caustic taste and slight odour, soluble in most organic solvents, but only sparingly in water (Bollard, G.P. 25578; J.S.C.I. 1897, **16**, 632; B.P. 27527, 1896). Therapeutically similar to guaiacol. Another *guaiacyl phosphite*, m.p. 59°, is described by Dupuis (Compt. rend. 1910, **150**, 622).

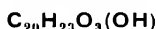
*Guaiacyl phosphate*,  $(\text{C}_6\text{H}_4\text{OMe})_3\text{PO}_4$ , is prepared by the interaction of phosphorus oxychloride and the sodium derivative of guaiacol. It forms colourless crystals; m.p. 98°, insoluble in water and alcohol, but soluble in ether, chloroform and acetone. It has been proposed as an intestinal antiseptic.

A number of other phosphorus compounds of

guaiacol are described by Auger and Dupuis (Compt. rend 1908, **146**, 1151), and by Dupuis (*ibid.* 1910, **150**, 622; cf. F.P. 781019 (1934); G.P. 629952; U.S.P. 2023551 (1935) Smith, Engel and Stohman discuss the toxicity of guaiacyl phosphate preparations (Nat. Inst. Health Bull. 1932, No. 160, 1).

**GUAIAACUM RESIN.** This resin is obtained by extraction with alcohol from the wood of *Guaiacum officinale* or *G. sanctum*, members of the family Zygophyllaceae. It is used to a small extent in medicine, but not to the extent it was some years ago, when it enjoyed an exaggerated reputation as a specific for gout and rheumatism. It occurs in round or ovoid tears, or in large blocks, breaking with a vitreous fracture. Thin fragments are yellowish-green to reddish-brown.

A number of resin acids in guaiacum have been described, including guaiaretic acid,



$\alpha$ - and  $\beta$ -guaiacetic acids,  $\text{C}_{20}\text{H}_{22}\text{O}_3(\text{OH})_2$ , and guaiacic acid,  $\text{C}_{21}\text{H}_{10}\text{O}_4(\text{OH})_3$ . For details of these, see Dobner and Lueker (Arch. Pharm. 1926, **234**, 590). Further evidence is necessary to establish the individuality of these acids, the formulae of which are probably derived only from combustion data.

Good quality guaiacum resin should contain about 90% of matter soluble in alcohol, and ash from 3.5 to 5%. The acid value of the resin varies from 45 to 55, and ester value from 120 to 140.

Fresh alcoholic extract of guaiacum resin is a noted biochemical reagent for peroxidases; for a critical account, see Hawk, Bergheim and Coles, "Practical Physiological Chemistry," 11th ed., 1938, p. 393. Although it has been used for the purpose, guaiacum is not a specific test for blood stains (see Haldane, "Enzymes," 1930, p. 10).

E. J. P.

"**GUAIAKINOL**," Guaiachinol, the guanine derivative of bromoguaiacol.

"**GUAIAMAR**," monoglyceryl ether of guaiacol.

**GUAIARETIC ACID** (v. GUAIAACUM RESIN).

**GUAIASANOL** (v. GUAIACOL).

**GUAIAZULENE** (v. GUAIAOL).

**GUAICAMPHOL**. Camphoric ester of guaiacol.

**GUAIENE** (v. GUAIAOL).

**GUAIAOL**. The crystalline sesquiterpene alcohol, *guaiol*,  $\text{C}_{16}\text{H}_{26}\text{O}$ , m.p. 93°, b.p. 147–148°/9 mm.,  $n_D^{100}$  0.9074,  $n_D^{20}$  1.4716,  $[\alpha]_D^{20}$  –29.8° (in alcohol), is a constituent of Guaiacum wood oil (from the wood of the tree, *Bulnesia sarmienti* Lorenz) (Schimmel's Report, 1892, II, 42) and occurs also in the oils from *Callitris glauca* (Baker and Smith, "Pines of Australia," 1910, pp. 63, 118), *C. intratropica* (Trikojus and White, J. Proc. Roy. Soc. New South Wales, 1935, **68**, 177) and from *Gonystylus miquelianus* (Eyken, Rec. trav. chim. 1906, **25**, 44). Guaiol is a dioleylic tertiary alcohol, its structure having been determined by Plattner *et al.* (Helv. Chim. Acta, 1940, **23**, 897; 1941, **24**, 191, 1164). It yields on catalytic hydrogenation the alcohol, *dihydroguaiol*, m.p. 79–80°, Ruzicka and Haagen-

Smit, *ibid.* 1931, **14**, 1131) or the hydrocarbon, *tetrahydroguaiene*, b.p. 118–119°/17 mm.,  $d_4^{20}$  0.8806,  $n_D$  1.47840,  $[\alpha]_D +10.31^\circ$  (Semmler and Risse, Ber. 1913, **46**, 2305). On dehydration it yields a hydrocarbon or mixture of hydrocarbons known as *guaiene*, b.p. 128–130°/12 mm.,  $d_4^{19}$  0.9115,  $n_D$  1.5022,  $\alpha_D -16.8^\circ$  (Ruzicka, Pontalti and Balas, Helv. Chim. Acta, 1923, **6**, 862), from which by dehydrogenation with sulphur the azulene, *guiazulene*, b.p. 164°/11 mm.,  $d_4^{19}$  0.9759, results (Ruzicka and Rudolph, *ibid.* 1920, **9**, 140; St. Pfau and Plattner, *ibid.* 1936, **19**, 866). The products formed by the oxidation of guaiol with potassium permanganate and with ozone have been studied by Semmler and Mayer (Ber. 1912, **45**, 1391), Ruzicka and Haagen-Smit (*l.c.* p. 1122), and by Trikojus and White (*l.c.*). The main oxidation product with either reagent is a *dihydroxy-oxide*,  $\text{C}_{15}\text{H}_{26}\text{O}_3$ , m.p. 218°.

J. L. S.

**GUAIIYL ACETATE.** Guaiol (*q.v.*) has a slight odour suggestive of tea-roses, and is identical with the alcohol isolated from Champaca wood and formerly known as champacal (Merk, Arch. Pharm. 1893, **231**, 123; Wallach and Tuttle, Annalen, 1894, **279**, 391). The acetate has a definite tea-rose odour, and the following characteristics,  $d_4^{15.5}$  0.988,  $n_D^{20}$  1.4890,  $[\alpha]_D -2.8^\circ$ ; ester value 210–220.

E. J. P.

**GUANASE** (v. Vol. IV, 315a).

"**GUANICAINE**" (v. Vol. I, 120d).

**GUANIDINE**,  $\text{HN:C}(\text{NH}_2)_2$ , occurs in small quantities in etiolated vetch seedlings, 3 kg. of dried material yielding 1 g. of the nitrate (Schulze, Ber. 1892, **25**, 658); in beet juice (Lippmann, *ibid.* 1896, **29**, 2651); in an edible mushroom, *Boletus edulis* (Winterstein *et al.*, Landw. Vers.-Stat. 1913, **79–80**, 541); and in the developing embryo chick (Burns, Biochem. J. 1916, **10**, 263). Guanidine and methylguanidine are found in urine, blood serum and other biological fluids, the quantities being increased in certain pathological conditions (see Burns and Sharpe, Quart. J. Exp. Physiol. 1916, **10**, 345; Minot and Dodd, Amer. J. Dis. Children, 1933, **46**, 522).

Guanidine was first prepared by Strecker (Annalen, 1861, **118**, 159) by oxidising guanine with potassium chlorate and hydrochloric acid; it is also obtained in small quantity by oxidising egg albumen with potassium permanganate, or gelatin with barium or calcium permanganate (Lossen, *ibid.* 1880, **201**, 369; Boudet, J. Pharm. Chim. 1857, [iii], **31**, 32; Kutscher and Zickgraf, Sitzungsb. K. Akad. Wiss. Berlin, 1903, **28**, 624); it is formed synthetically (1) by heating biuret and hydrogen chloride at 160–170° (Finckh, Annalen, 1862, **124**, 332); (2) from chloropierin and alcoholic ammonia at 100° (Hofmann, Ber. 1868, **1**, 145); (3) from ethyl orthocarbonate and aqueous ammonia at 150° (Hofmann, Annalen, 1866, **139**, 111); (4) from carbonyl chloride and ammonia (Bouchardat, Compt. rend. 1869, **69**, 961); (5) from urea and ammonia under dehydrating conditions; ammonia and carbon dioxide or salts derived from them may be used instead of urea; finely divided nickel, aluminium, alumina or manganese

dioxide have been proposed as catalysts for the reaction, which takes place at 250–300° under pressure or at lower temperatures in the presence of a non-aqueous solvent (Sander, G.P. 527237); (6) from ammonium chloride and alcoholic cyanamide at 100° (Erlenmeyer, *Annalen*, 1868, 146, 259), modifications of this method using dicyanodiamide and various ammonium salts are frequently used for the preparation of guanidine salts; (7) by the hydrolysis of dicyanodiamide with mineral acid, each molecule giving 1 mol. of guanidine (Davis, J. Amer. Chem. Soc. 1921, 43, 669), (8) by the oxidation of dicyanodiamidine (Baumann, Ber. 1874, 7, 1766; cf. the action of *aqua regia*, Ulpiani, G.P. 209431); (9) from cyanogen iodide and alcoholic ammonia at 100° (Bannow, Ber. 1871, 4, 161). Reduction of tetranitromethane with nickel-zinc and HCl yields guanidine hydrochloride (Rakshat, J. Amer. Chem. Soc. 1914, 36, 1221). Stähler obtained this salt from  $\text{CCl}_4$  and  $\text{NH}_3$  at 140° in presence of Cu and I (Ber. 1914, 47, 909). Hydrogenation of carbamidoimidoazide nitrate (Hantzsch and Vagt, *Annalen*, 1901, 314, 339) in the presence of colloidal palladium gives guanidine and nitrogen (Wienhaus and Ziehl, Ber. 1932, 65 [B], 1461).

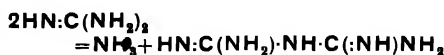
Guanidine, in the form of its salts, is usually prepared by modifications of Erlenmeyer's ((6) *supra*) or by the following method. Ammonium thiocyanate is heated for 20 hours at 180–190°, and the melt is extracted with water. The extract concentrated and the guanidine thiocyanate allowed to crystallise (Delitsch, J. pr. Chem. 1873, [ii], 8, 240; 1874, [ii], 9, 2; Volhard, *ibid.*, 9, 15; Krall, J.C.S. 1913, 103, 1378 Sharpe, J. Biol. Chem. 1917, 28, 399).

Glund *et al.* (Ber. Ges. Kohlentech. 1931, 4, 21; F.P. 728156; G.P. 568401) lead ammonia gas through molten ammonium thiocyanate at 170–180°. In Gockel's modification a metallic salt, e.g. of lead, is present (Angew. Chem. 1935, 48, 430). Schöpf and Klapproth have reported a violent explosion (*ibid.* 1936, 49, 23). The best methods of preparing guanidine salts depend on heating the corresponding ammonium salts with dicyanodiamide (Rathke, Ber. 1885, 18, 3107). Thus, Werner and Bell describe the preparation in 90% yield of the thiocyanate by this method (J.C.S. 1920, 117, 1133), and Davi (Org. Synth. 1927, 7, 46) similarly prepared the nitrate. Davis recommends heating dicyanodiamide and ammonium nitrate. Smith, Sabetts and Steinbach (Ind. Eng. Chem. 1931, 23, 1124) state the optimum conditions. Preparations guanidine sulphate from dicyanodiamide, *see* Levene and Senior, J. Biol. Chem. 1916, 25 623; Lidholm, Ber. 1913, 46, 156; Caro, Z. angew. Chem. 1910, 23, 2405; guanidine phosphate, Jones and Aldred, Ind. Eng. Chem. 1936 28, 272; guanidine salts from metallic cyanamides, G.P. 586446, 600869, and for the mechanism of the process, Gockel, Angew. Chem. 1934, 47, 555.

Guanidine is a deliquescent crystalline solid readily soluble in alcohol and water; it is volatile and strongly alkaline, absorbs carbon dioxide from the air, and forms crystalline salts. According to e.m.f. measurements it is a stronger base than any other organic nitrogenous base

recorded (Hall and Sprinkle, J. Amer. Chem. Soc. 1932, 54, 3469). The ultra-violet absorption spectrum shows only end absorption Graubner, Z. ges. exp. Med. 1928, 63, 527). Guanidine is decomposed into ammonia and urea on boiling with barium hydroxide solution or dilute sulphuric acid (Ossikowsky, Bull. Soc. chim. 1872, [ii], 18, 161; Baumann, Ber. 1873, i, 1376); and is completely decomposed into carbon dioxide and ammonia by heating with concentrated acids or alkalis. Guanidine is decomposed, evolving two-thirds of its nitrogen when mixed with sodium hypochlorite or hypomrite (Fenton, J.C.S. 1879, 35, 14; Von Jordier, *Monatsh.* 1926, 47, 327). When chlorinated at 0° in slightly acid solution buffered with NaOAc and AcOH, guanidine is converted into N-chloroazodicarbamides (U.S.P. 2016257). Nitrous acid reacts with guanidine with liberation of nitrogen but only in the presence of strong acid (Hynd and MacFarlane, Biochem. J. 1926, 20, 1264). Cyanamide is formed when nitrous fumes are passed into aqueous guanidine sulphate (Bancroft and Belden, J. Physical Chem. 1931, 35, 2684). Guanidine and those of its derivatives containing a free amino-group react, on warming, with diacetyl or generally with compounds containing the grouping  $\text{CO}\cdot\text{CO}\cdot\text{CH}_2$ — with the formation of a violet coloration which has been made the basis for a colorimetric method of determining creatine and arginine (Lang, Z. physiol. Chem. 1932, 208, 273). Guanidine forms condensation products with dicarboxylic acids (Traube, Ber. 1893, 26, 2551; Ruheman and Stapleton, J.C.S. 1900, 77, 805; Kaess and Gruszkiewicz, Ber. 1902, 35, 3600); with  $\beta$ -ketonic acids (Jaeger, *Annalen*, 1891, 262, 365); with  $\beta$ -liketones (Evans, J. pr. Chem. 1892, [ii], 45, 489; Wense, Ber. 1886, 19, 761); with malononitrile (Merck, G.P. 165692); with ethyl cyanoacetate (Traube, G.P. 115253). Guanidine reacts with mustard oils to form guanylthiouras,  $\text{R}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NH})\text{NH}_2$  (Slotta, *Tschesche und Dressler*, Ber. 1930, 63 [B], 208). Glycine ester reacts with 2 mol. of anhydrous guanidine giving glycoeyguanidine (Abderhalden and Sichel, Z. physiol. Chem. 1928, 173, 51). Guanidine forms compounds with sugars containing 3 mol. of sugar and 1 mol. of guanidine; these exhibit mutarotation and have a lower optical activity than the sugars from which they are derived (Morrell and Bellars, J.C.S. 1907, 91, 1010; Przylecki *et al.*, Biochem. Z. 1935, 277, 420, 424; cf. Giedroyć, Cichočka and Mystkowski, *ibid.* 1935, 281, 422). Combination with proteins also occurs under suitable pH conditions. Thus, guanidine combines with ovalbumin and gelatin above the isoelectric points, with casein and globulin below their isoelectric points (Petrunkin, J. Gen. Physiol. 1927, 11, 101; Przylecki, Mystkowski and Niklewski, Biochem. Z. 1933, 262, 260).

When guanidine hydrochloride is heated at 180°, ammonia is evolved and *biguanide* is formed, the reaction being similar to the formation of biuret from urea:



In its physiological action, guanidine is highly toxic; when fed to rabbits, it causes a considerable fall in the blood sugar, convulsions and death (Frank, Nothmann and Wagner, Arch. exp. Path. Pharm. 1926, **115**, 55). Doses smaller than poisonous ones were in rabbits excreted unchanged in the urine (Pommerrenig, Beitr. chem. Physiol. Path. 1902, **i**, 561; Garino, Arch. Farm. sperim. 1916, **22**, 229, from Chem. Zentr. 1916, **II**, 1047). For other physiological data, see Dominguez, Proc. Soc. Exp. Biol. Med. 1927, **25**, 57; Hurst and Hurst, J. Path. Bact. 1928, **31**, 303; Camis, J. Physiol. 1909, **39**, 73; Fuhrer, Arch. exp. Path. Pharm. 1920, **88**, 179; Langley, J. Physiol. 1916, **50**, 419; Meighan, *ibid.* 1917, **51**, 51). Although guanidine does not appear to be a normal oxidation product of arginine in the body (Pommerrenig, *loc. cit.*), guanidine intoxication occurs in certain clinical conditions (Minot and Dodd, Amer. J. Dis. Children, 1933, **46**, 522). Many derivatives of guanidine, e.g. 1-guanido-4-aminobutane ("Agmatine"), the corresponding derivative of decane ("Synthalin"), the compound



("Acoine"), exhibit a marked insulin-like activity which has been applied in a few instances to the treatment of mild cases of *diabetes mellitus* (Frank, Nothmann and Wagner, Klin. Wochschr. 1926, **5**, 2100; Cannavò, Arch. Farm. sperim. 1927, **44**, 49; 45, 218; Kumagai, Kawai and Shikimami, Proc. Imp. Acad. (Japan), 1928, **4**, 23; Gessner, Arch. exp. Path. Pharm. 1930, **147**, 366; Harwood, Iowa State Coll. J. Sci. 1932, **6**, 431). Small quantities of guanidine, 0.01%, are injurious to chlorophyllous plants, whilst fungi utilise it as a source of nitrogen but not of carbon (Kawakita, Bull. Coll. Agr. Tokyo, 1904, **6**, 181; Kossawitz, Chem. Zentr. 1913, **1**, 1279). For its significance in plant physiology, see Taubock and Winterstein, in G. Kleim, Handb. Pflanzenanalyse, 1933, **4**, 190; Chem. Zentr. 1933, **II**, 3321.

**Tests and Estimation.**—Many salts of guanidine give a yellowish-white flocculent precipitate with Nessler's reagent, even at a dilution of 0.01% (Schulze, Ber. 1892, **25**, 661). Arginine gives a similar precipitate (Barger, "Simpler Natural Bases," 1914, 164; nephelometric determination of small quantities of guanidine, Rittmann, Biochem. Z. 1926, **172**, 36). A reagent made from 10% solutions of sodium nitroprusside and potassium ferricyanide mixed with sodium hydroxide just before use gives an intense red coloration with guanidine and its mono- and disubstituted derivatives. The guanidines are first separated as phosphotungstates or adsorbed on "norit" (Weber, Proc. Soc. Exp. Biol. Med. 1927, **24**, 712; Paffner and Myers, *ibid.* 1926, **23**, 830; J. Biol. Chem. 1930, **87**, 345; Ellis, Biochem. J. 1928, **22**, 353; Weber, J. Biol. Chem. 1928, **78**, 465).

A test developed by Sullivan has also been used for the colorimetric estimation of guanidine. To guanidine in aqueous or 0.1*N*-hydrochloric acid solution is added a 1% solution of sodium 1:2-naphthoquinone-4-sulphonate and *N*-NaOH. After heating to 90°C for 1 minute

and cooling again, the solution is strongly acidified with hydrochloric acid. Addition of concentrated nitric acid now causes the formation of a red coloration or brown precipitate of 4-guanido-1:2-naphthoquinone (Sullivan, Proc. Soc. Exp. Biol. Med. 1935, **33**, 106; Sullivan and Hess, J. Amer. Chem. Soc. 1936, **58**, 47). Interference due to ammonia, methylamine, indole or benzidine can be eliminated by their removal beforehand. Certain synthetic derivatives of guanidine interfere (Braun and Rees, J. Biol. Chem. 1936, **114**, 415), but these may be rendered inactive by addition of a little hydroxylamine immediately before acidification (Sullivan, *ibid.* 1936, **116**, 233).

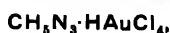
The separation of guanidines from creatine and creatinine by adsorption on "Dowcil," a sodium aluminium silicate, has been suggested by Saunders (Biochem. J. 1932, **26**, 801). The separation of guanidine and methylguanidine can be effected by means of  $\beta$ -naphthalenesulphonyl chloride and depends on the fact that, under standardised conditions, methylguanidine does not react with this reagent (Hess and Sullivan, J. Amer. Chem. Soc. 1935, **57**, 2331).

In the estimation of guanidine by precipitation with picric acid, the salt is dried at 110° and weighed (Vozárik, Z. angew. Chem. 1902, **15**, 670). Picrolonic acid has been used in preference to picric acid since the precipitates are not contaminated with creatinine (Kuen, Biochem. Z. 1927, **187**, 283). Flavonic acid can be used similarly (Muller, Z. physiol. Chem. 1932, **209**, 207). Guanidine phosphotungstate is soluble (22.8 parts) in 100 parts of a mixture of acetone (4 vol.) with water (3 vol.) (Wechsler, *ibid.* 1911, **73**, 141; Drummond, Biochem. J. 1918, **12**, 5). 2-Nitro-1:3-indanedione forms a guanidine salt, m.p. about 258°, which is of use in the identification of guanidine (Wanag and Lode, Ber. 1937, **70** [B], 547). Choline and guanidine may be detected in organs by means of a histochemical test described by Hirose (Mitt. Med. Ges. Tokio, 1931, **43**, 888; Chem. Zentr. 1931 **1**, 654; Amer. Chem. Abstr. 1932, **26**, 3812).

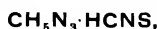
For the identification of the arylguanidines, used for the vulcanisation of rubber, by a colour reaction with cobalt oleate, see Shimada (J. Soc. Chem. Ind. Japan, 1933, **36**, Suppl. binding 82), and for their estimation by titration with hydrochloric acid, see Mogoricheva and Korsunskaja, J. Rubber Ind. U.S.S.R. 1933, **10**, 341; Minatoya, Nagai and Aoe, J. Soc. Rubber Ind. Japan, 1934, **7**, 134; 1935, **8**, 328; Kuznetsov, J. Chem. Ind. (Moscow), 1935, **12**, 1265; Humphrey, Ind. Eng. Chem. [Anal.], 1936, **8**, 153 (estimation as picrate after hydrolysis).

**Salts.**—Guanidine forms crystalline salts with mineral and organic acids, and also characteristic double salts. The *hydrochloride*, or *guanidininium chloride*,  $\text{CH}_6\text{N}_3\text{Cl}$ , crystallises in the orthorhombic system (Theilacker, Z. Krist. 1931, **76**, 303) and forms double salts with *mercuric chloride*,  $\text{CH}_6\text{N}_3\text{Cl} \cdot 2\text{HgCl}_2$  (Byk, J. pr. Chem. 1879, [ii], 20, 233) and *platinic iodide* (Datta and Ghosh, J. Amer. Chem. Soc. 1914, **36**, 1017). The *hydrobromide*,  $\text{CH}_6\text{N}_3\text{Br}$ , forms orthorhombic bipyramidal crystals (Theilacker, Z. Krist. 1935, **90**, 256). Both the bromide and iodide form addition compounds with *mercuric*

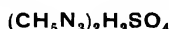
cyanide of the type  $\text{CH}_5\text{N}_3\text{I}\cdot\text{Hg}(\text{CN})_2$ , m.p.  $261^\circ$  (decomp.). The *chloroaurate*,



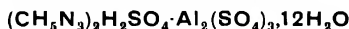
forms deep yellow, sparingly soluble needles (Hofmann, Ber. 1868, 1, 146); the *chloroplatinate*,  $(\text{CH}_5\text{N}_3)_2\text{H}_2\text{PtCl}_6$ , yellow needles soluble in water, sparingly so in alcohol (Strecker, Annalen, 1861, 118, 160); the *platinithiocyanate*,  $(\text{CH}_5\text{N}_3)_2\text{H}_2\text{Pt}(\text{CNS})_6$ , forms beautiful red crystals which blacken at  $170\text{--}175^\circ$  (Guareschi, Chem. Zentr. 1891, II, 620). For the *palladochloride*, see Gutbier and Fellner, Z. anorg. Chem. 1916, 95, 128. The *thiocyanate*,



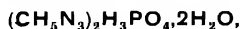
has m.p.  $118^\circ$  and 100 parts of water dissolve 134.9 parts at  $15^\circ$  (Engel, Bull. Soc. chim. 1885, [ii], 44, 424). The *azide*,  $\text{CH}_5\text{N}_3\cdot\text{HN}_3$ , m.p.  $93\text{--}5^\circ$ , is formed by double decomposition between the chloride and silver azide. When treated with carbon disulphide, it forms guanidine azido-dithiocarbonate,  $\text{CH}_5\text{N}_3\cdot\text{HSCSN}_4$  (Craik, Berger and Browne, J. Amer. Chem. Soc. 1934, 56, 2380). The *nitrate*,  $\text{CH}_5\text{N}_3\cdot\text{HNO}_3$ , crystallises in large plates, m.p. (corr.)  $217^\circ$ ; 25.6 parts dissolve in 100 parts of water at  $20^\circ$  (Smith, Sabetta and Steinbach, Ind. Eng. Chem. 1931, 23, 1124). For the preparation of the nitrate from the thiocyanate, see Jousseim, Bull. Soc. chim. 1880, [ii], 34, 497. The *nitrite*,  $\text{CH}_5\text{N}_3\cdot\text{HNO}_2$ , forms glittering prisms, m.p.  $76\text{--}78.5^\circ$  (Lossen, Annalen, 1891, 265, 129). The *sulphate*,



(Bodewig, J. Ann. Physik, 1876, 157, 125), forms a double salt with *aluminium sulphate*,



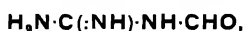
(Ferraboschi, Proc. Camb. Phil. Soc. 1908, 14, 471). The *carbonate*,  $(\text{CH}_5\text{N}_3)_2\text{H}_2\text{CO}_3$ , prisms, m.p.  $197^\circ$  (Schroder, Ber. 1880, 13, 1072); Burgers (Proc. Roy. Soc. 1927, A, 116, 553) described uniaxial, optically active crystals in which the activity was attributed to a special arrangement of the atoms within the unit structure. The *trithiocarbonate*,  $(\text{CH}_5\text{N}_3)_2\text{H}_2\text{CS}_3$ , is prepared by heating the free base with carbon disulphide for 2 hours at  $100^\circ$  (Strack, Z. physiol. Chem. 1929, 180, 198). The *metaphosphate*,  $\text{CH}_5\text{N}_3\cdot\text{HPO}_3$ , forms a fine crystalline precipitate (Pohl, *ibid.* 1889, 13, 296). *Diguanidine phosphate*,



is obtained by stirring the thiocyanate with silver phosphate and 20% phosphoric acid at  $50^\circ$  and evaporating to dryness (G.P. 614818). The *diethylpyrophosphate* results from the action of ethyl metaphosphate on the carbonate in dry chloroform (Plimmer and Burch, J.C.S. 1929, 279). The *hypophosphate* has been prepared and its magnetic susceptibility ( $-0.41$  at  $18\text{--}20^\circ$ ) determined (Bell and Sugden, *ibid.* 1933, 48). The *chlorate*,  $\text{CH}_5\text{N}_3\cdot\text{HClO}_3$ , m.p.  $100\text{--}101^\circ$  (cf. the decomposition temperature  $148^\circ$  given by Datta and Choudhury, J. Amer. Chem. Soc.

1916, 38, 1079), is less stable than the *perchlorate*,  $\text{CH}_5\text{N}_3\cdot\text{HClO}_4$ , m.p.  $245\text{--}246^\circ$  (Mieczwicz, Przemysl Chem. 1926, 10, 56, 136). According to Mazzucchelli and Rossi (Gazzetta, 1927, 57, 383), the perchlorate cannot be exploded with a hammer and when heated in the open it fuses and volatilises. The *mono*-, *di*- and *tri-chromates* are prepared by the action of chromic acid on the carbonate. The *monochromate* forms triclinic, the *di*- and *tri-chromates* monoclinic crystals (Swaryczewski, Bull. Acad. Polonaise, Classe sci. math. nat. 1934, A, 246). Guanidine forms salts with a number of chromium complexes, e.g. the *reineckate*,  $[(\text{SCN})_2\text{Cr}(\text{NH}_3)_2]^-[\text{CH}_5\text{N}_3]^+$  (Carlssohn and Rathmann, J. pr. Chem. 1936, [ii], 147, 29, solubility data are given). The *acetate* forms shining needles, m.p.  $229\text{--}230^\circ$  (Ostrogovich, Gazzetta, 1897, 27, i, 223; cf. Wieland *et al.*, Annalen, 1933, 507, 226). The *dioxalate*,  $\text{CH}_5\text{N}_3\cdot\text{C}_2\text{H}_2\text{O}_4\cdot\text{H}_2\text{O}$ , is sparingly soluble (Strecker, *l.c.*). The salt with acetylglycine has m.p.  $105\text{--}110^\circ$ . With 3:5-dinitrobenzoyl chloride in the presence of alkali, guanidine gives a di-3:5-dinitrobenzoyl derivative which is insoluble in sodium hydroxide (Saunders, Biochem. J. 1934, 28, 580). The *picrate*,  $\text{CH}_5\text{N}_3\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$  is a sparingly soluble, yellow, crystalline salt, m.p.  $333^\circ$ ; 1 part dissolves in 2,630 parts of water at  $9^\circ$  (Emich, Monatsh. 1891, 12, 24). The precipitation of guanidine picrate is prevented by nucleic acid, owing to the formation of a more soluble complex picrate (White, Trans. Roy. Soc. Canada, 1926, 20, Sect. V, 321). According to Von Cordier (Chem. Zentr. 1906, I, 340), guanidine picrate (cf. *supra*), exists in two stereoisomeric forms which are identical in specific gravity and electrical conductivity but differ in solubility. The *p-toluenesulphonate* has m.p.  $206^\circ$ , and the  *$\beta$ -naphthalenesulphonate*, m.p.  $259^\circ$  (Remsen and Garner, Amer. Chem. J. 1901, 25, 173). The *picrolonate*,  $\text{CH}_5\text{N}_3\cdot\text{C}_{10}\text{H}_7\text{O}_5\text{N}_4$ , is soluble in alcohol (Schenck, Z. physiol. Chem. 1905, 44, 427); the *m-bromopicrolonate* decomposes at  $275^\circ$  (Zimmermann and Cuthbertson, *ibid.* 1932, 205, 38). Many guanidinium salts of inorganic *iso*- and hetero-poly acids have been prepared (Gutbier, Mehler and Ottenstein, Z. anorg. Chem. 1914, 89, 313, 333, 343; Rosenheim *et al.*, *ibid.* 1913, 79, 292; 1914, 89, 224; 1915, 91, 75; 1930, 193, 64; 1932, 204, 342; Ber. 1911, 44, 1865; Z. Elektrochem. 1911, 17, 694; Fernandes *et al.*, Atti R. Accad. Lincei, 1927, [vi], 5, 339; 1927, [vi], 6, 102; 1928, [vi], 7, 496; Gazzetta, 1926, 56, 655; Brukl and Hahn, Monatsh. 1932, 59, 194; Schramm, Z. anorg. Chem. 1927, 161, 231; Weinland and Friede, Arch. Pharm. 1928, 266, 353).

**Acyl Derivatives.**—*Formylguanidine*,

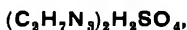


has m.p.  $178^\circ$  (decomp.); *acetylguanidine*, m.p.  $185^\circ$ , *hydrochloride*, m.p.  $145^\circ$  (Korndorfer, Arch. Pharm. 1903, 241, 449, gives m.p.  $142^\circ$ ). (See also Traube, Ber. 1910, 43, 3586; Pierrow, Compt. rend. 1910, 151, 1364; Wheeler and Johnson, Amer. Chem. J. 1901, 26, 417; Andreasch, Monatsh. 1926, 46, 639.)

*Allylmalonylguanidine*, m.p. 265–266°, crystallises from acetic acid in hexagonal plates (Johnson and Hill, *Amer. Chem. J.* 1911, **48**, 537). For *guanidino-glycylglycine* and the introduction of guanidine into the polypeptide molecule, see Clementi, *Gazzetta*, 1915, **45**, i, 56, ii, 276.

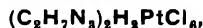
**Alkyl and Aryl Derivatives.**—*Methylguanidine*,  $\text{HN}:\text{C}(\text{NH}_2)\text{NHMe}$ , has been isolated from muscle (Gulewitsch, *Z. physiol. Chem.* 1906, **47**, 471; Ewins, *Biochem. J.* 1916, **10**, 163; Smorodintzev and Adova, *Z. physiol. Chem.* 1928, **181**, 77; Komarow, *Biochem. Z.* 1929, **211**, 320) and is considered by Mann to be a natural constituent of muscle (*ibid.* 1934, **268**, 339). It has been found in milk (Muller, *Z. Biol.* 1920, **84**, 553). For its isolation from normal human urine, see Wada, *Acta Schol. Med. Univ. Imp. Kyoto*, 1930, **13**, 187, and from that of dogs, see Koch, *J. Biol. Chem.* 1913, **15**, 313; for its determination in blood, see Zappacosta, *Boll. Soc. Ital. Biol. sperim.* 1935, **10**, 705; see also the methods of determining guanidine, many of which are applicable to its alkyl derivatives. It can be prepared by several of the methods used for guanidine if methylamino is substituted for ammonia, e.g. Erlenmeyer's and Werner and Bell's methods (Erlenmeyer, *Ber.* 1870, **3**, 896; B.P. 279884; *Canad. P.* 281121; *Amer. Chem. Abstr.* 1929, **23**, 3443; Philippi and Morsch, *Ber.* 1927, **60** B, 2120). The Rathke synthesis, consisting of the treatment of alkylisothiourea salts with an amine, is general and applicable also to the preparation of polyalkyl-substituted derivatives (Lecher, *Z. physiol. Chem.* 1928, **176**, 43; *Canad. P.* 276107; Piovano, *Gazzetta*, 1928, **58**, 245; Phillips and Clarke, *J. Amer. Chem. Soc.* 1923, **45**, 1755; Smith, *ibid.* 1929, **51**, 476). A special method of preparation of methylguanidine is by boiling creatine with mercuric or lead oxide and dilute sulphuric acid (Dessaignes, *Annalen*, 1854, **92**, 407; 1856, **97**, 340). For separation of guanidine and methylguanidine (see p. 144c). Methylguanidine gives a characteristic red colour (Sagakuichi reaction) when treated, in alkaline solution, with  $\alpha$ -naphthol and sodium hypochlorite. This reaction may be used for its colorimetric determination if the concentration is greater than 50 mg. per litre (Kuen, *Biochem. Z.* 1927, **187**, 283). The alkaline nitroprusside-ferri-cyanide reagent (p. 144b) is also applicable to the colorimetric estimation of methylguanidine (Piffner and Myers, *Proc. Soc. Exp. Biol. Med.* 1926, **23**, 830).

Methylguanidine is a strongly basic, volatile, deliquescent crystalline substance which readily decomposes; it decolorises permanganate, and liberates ammonia and methylamine on heating with potassium hydroxide. For the preparation of the *chloride* and its conversion to other salts, see Traube and Gorniak, *Amer. Chem. Abstr.* 1929, **23**, 3443. The *sulphate*,



crystallised from water, has m.p. 238°; the *nitrate*, from ethyl alcohol, m.p. 148–149°; the *nitrite*, m.p. 150° and the *formate*, m.p. 122°. The *oxalate*,  $(\text{C}_2\text{H}_7\text{N}_3)_2\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , is cry-

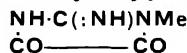
stalline and soluble in water. The *chloroaurate*,  $\text{C}_2\text{H}_7\text{N}_3 \cdot \text{HAuCl}_4$ , forms yellow crystals, m.p. 108–200°; the *platinichloride*,



yellowish-red prisms, sintering at 186–187° and m.p. 194–195° (Schenck, *Arch. Pharm.* 1909, **247**, 466; Schenck and Kirchhof, *Ber.* 1927, **60** [B], 2412). The *reineckate*,



has m.p. 228–230° (Smorodintzev, *Z. physiol. Chem.* 1930, **189**, 7). The *picrate* crystallises from water in two distinct modifications, yellow plates or needles, m.p. 201.5° (Gulewitsch, *l.c.*). The *picolonate*,  $\text{C}_2\text{H}_7\text{N}_3 \cdot \text{C}_{10}\text{H}_6\text{O}_5\text{N}_4$ , melts at 291° (Wheeler and Jamieson, *J. Biol. Chem.* 1904, **4**, 111). *Acetylmethylguanidine* is formed by warming the base with ethyl acetate; it has m.p. 171–172°. *Benzoylmethylguanidine*, prepared similarly, has m.p. 156°; hydrochloride, m.p. 220–221°. *Oxalymethylguanidine*,



m.p. 205–207°, is formed from the base and ethyl oxalate in alcoholic solution.

Alkyl derivatives of guanidine containing higher alkyl groups and also polysubstituted derivatives are usually prepared either by Erlenmeyer's or Rathke's method. For the preparation from alkylisothioureas of mono-substituted guanidines with alkyl groups higher than methyl, see Schenck and Kirchhof, *Z. physiol. Chem.* 1926, **158**, 90; *Ber.* 1927, **60** [B], 2412; Piovano, *Gazzetta*, 1928, **58**, 245; and *Amer. Chem. Abstr.* 1933, **27**, 1867, and for Erlenmeyer's method, B.P. 279884; *Canad. P.* 281121; G.P. 494918; B.P. 286196; also Davis and Elderfield, *J. Amer. Chem. Soc.* 1932, **54**, 1199. For polyalkylguanidines, see Klingner, *Z. physiol. Chem.* 1926, **155**, 206; Lecher and Demmler, *ibid.* 1927, **167**, 163; Schenck and Kirchhof, *Ber.* 1927, **60** [B], 2412; Schotte, Prieve and Roescheisen, *Z. physiol. Chem.* 1928, **174**, 119; Davis and Elderfield, *l.c.*; B.P. 285873; and for peralkylated (pentasubstituted) guanidines, see Lecher *et al.*, *Annalen*, 1927, **455**, 139; U.S.P. 1766755.

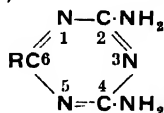
*$\alpha$ -Phenylguanidine*,  $\text{NH}:\text{C}(\text{NH}_2)\text{NHPh}$ , is conveniently prepared by heating aniline with methylisothiourea sulphate until evolution of mercaptan ceases, it is purified by conversion to the carbonate which is only slightly soluble in cold water. The free base, m.p. 66–68°, crystallises in the monoclinic system, is soluble in alcohol and benzene and slightly soluble in water, ether and carbon tetrachloride, and absorbs carbon dioxide and water from the air.  *$\alpha$ -Phenylguanidine sulphate* forms monoclinic crystals, m.p. 205°, is soluble in water and slightly soluble in 95% alcohol; the *carbonate*, monoclinic crystals, m.p. 138–140°, is soluble in hot water; the *nitrate*, triclinic crystals, m.p. 118–119°, is soluble in hot water and alcohol but slightly in cold; the *picrate*, m.p. 218–220°, forms either orthorhombic or triclinic crystals insoluble in water, and the *chloro-platinate*, m.p. 196°, triclinic crystals is slightly



soluble in water (Smith, J. Amer. Chem. Soc. 1929, **51**, 476).  $\gamma$ -Benzoyl- $\alpha$ -phenylguanidine has m.p. 91–92°. For other arylguanidines, see Braun, J. Amer. Chem. Soc., 1933, **55**, 1280.

**Diarylguanidines** are much used as accelerators for the vulcanisation of rubber (Elley and Powers, India Rubber World, 1926, **75**, 143; Stoll, Gummi-Ztg. 1926, **41**, 193; diphenylguanidine phthalate, U.S.P. 1950067).  $\alpha$ -Derivatives may be prepared by desulphurising diarylthioureas in the presence of ammonia, e.g. with basic salts of lead, zinc, cadmium or tin (Naunton, Trans. Inst. Rubber Industry, 1926, **2**, 147, J.S.C.I. 1926, **45**, 376r; U.S.P. 1630769, 1642180, 1662626, 1669242, 1672431; B.P. 262155); or, in excellent yield, by the action of cyanogen chloride or bromide on anilines (Naunton, l.c.; U.S.P. 1639724, 1639725). For the preparation of *aa*-diarylguanidines, see Paulson, U.S.P. 1575865; Arndt and Rosenau, Amer. Chem. Abstr. 1918, **12**, 1187. For reviews on the preparation of diphenylguanidine, see Hutin, Caoutchouc and Gutta-percha, 1926, **23**, 13297; Drozdov, J. Chem. Ind. Russ. 1932, No. 7, 44. When aryl substituted guanidines are heated, rearrangements occur (Klingner, Z. physiol. Chem. 1926, **155**, 206). Additional references to substituted guanidines are: Strakosch, Ber. 1872, **5**, 692; Tatarinow, J.C.S. 1880, **38**, 233; Noah, Ber. 1890, **23**, 2190; Hofmann, *ibid.* 1869, **2**, 601; Fischer, *ibid.* 1897, **30**, 2414; Alway and Vail, Amer. Chem. J. 1902, **28**, 158; Kampf, Ber. 1904, **37**, 1681; Riedel, G.P. 66550; 104361; Schenck, Arch. Pharm. 1911, **249**, 463, 1912, **250**, 306.

**Guanamines**.—When the guanidine salts of the fatty acid series are heated at 220–230°, water and ammonia are eliminated and 2,4-diamino-*s*-triazines, formerly called *guanamines*, are formed, and afford excellent means of identifying volatile fatty acids (Haaf, J. pr. Chem. 1891, [iii], **43**, 75):



The same series of compounds and also the aryl derivatives are formed when dicyanodiamide is heated with amidines or their salts or with nitriles at 200–250° with or without alcohol (Ostrogovich, Atti. R. Accad. Lincei, 1911, [v], **20**, i, 182, 249; Gazzetta, 1930, **60**, 648; 1932, **62**, 317; Amer. Chem. Abstr. 1930, **24**, 5752; Guanamines are also obtainable from biguanide and nitriles but the yields are lower. *Acetoguanamine*, ( $\text{R}=\text{CH}_3$ ) (6-methyl-2,4-diamino-1,3,5-triazine), m.p. 265°.

**Chloroguanidine**,  $\text{CH}_3\text{ClN}_3$ , obtained by the action of bleaching powder solution on guanidine carbonate in ice-water, forms a pale yellow crystalline powder that decomposes at 150° (Kamenski, Ber. 1878, **11**, 1602).

**Bromoguanidine**,  $\text{CH}_3\text{BrN}_3$ , formed from equimolecular proportions of bromine and guanidine carbonate, crystallises in yellow needles. By the action of 3 mol. bromine on 1 mol. guanidine carbonate, the compound,  $\text{CH}_3\text{N}_2\cdot\text{HBr}\cdot\text{Br}_2$ , is formed, crystallising in

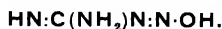
dark red prisms. The corresponding *iodine compound*,  $\text{CH}_3\text{N}_2\cdot\text{HI}\cdot\text{I}_2$ , crystallises in prisms the colour of iodine (Kamenski, l.c.).

$\alpha$ -Cyanoguanidine (*Dicyanodiamide*, *q.v.*). **Nitroguanidine**,  $\text{HN}=\text{C}(\text{NH}_2)\text{NH}\cdot\text{NO}_2$ , was first prepared by Jouselin (1877) by the action of fuming nitric acid and nitric oxide on guanidine nitrate, and called by him nitrosoguanidine. Pellizzari (Gazzetta, 1891, **21**, ii, 405) showed that it was the *nitro* compound and his results were confirmed by Thiele (Annalen, 1892, **270**, 1), who also prepared it by the action of fuming nitric acid and sulphuric acid on guanidine thiocyanate. It exists in two modifications which differ in crystal form and habit and slightly in solubility, but are otherwise identical. The two forms are not interconvertible by solution in water, and may be separated by fractional crystallisation from that solvent. Either compound, dissolved in sulphuric acid and poured into water, gives the  $\alpha$ -form. Neither appears to be an *act*-form or a stronger *pseudo*-acid than the other since their solubilities in 0.1N-KOH are essentially the same.  $\alpha$ -Nitroguanidine is most conveniently prepared in 92% yield by adding pure guanidine nitrate, ground to a uniform fineness, to 3 parts by weight of concentrated sulphuric acid cooled to below 0°. The reaction should not be prolonged for more than an hour, otherwise hydrolysis proceeds more rapidly than nitration (Smith, Sabetta and Steinbach, Ind. Eng. Chem. 1931, **23**, 1124). Davis (Organic Syntheses, 1927, **7**, 68) describes a similar method giving a yield of 73%. It crystallises from water in colourless needles resembling phthalic anhydride, m.p. 246°, varying with the rate of heating; 100 c.c. of water dissolve 0.271 g. at 19.5°. It is slightly soluble in ethyl acetate, acetone, ethyl alcohol, methyl alcohol and pyridine, but insoluble in benzene, toluene, chloroform, carbon tetrachloride, ether and carbon disulphide (Deverges, Rev. Chim. Ind. 1929, **38**, 265; Amer. Chem. Abstr. 1930, **24**, 350). The heat of combustion at constant pressure is +210.3 kg.-cal. and the heat of formation from its elements is +22 kg.-cal (Matignon, Compt. rend. 1892, **244**, 1432).  $\beta$ -Nitroguanidine is produced in variable amount, usually accompanied by the  $\alpha$ -form, by nitration of guanidine sulphate (mixed with  $(\text{NH}_4)_2\text{SO}_4$ ) which results from the hydrolysis of dicyanodiamide with sulphuric acid (Davis, Ashdown and Couch, J. Amer. Chem. Soc. 1925, **47**, 1063). The  $\beta$ -form crystallises from water in small thin elongated plates; for solubility curves of the two forms, see Davis, Ashdown and Couch, l.c. For the ultra-violet absorption, see Riegel and Buchwald, *ibid.* 1920, **51**, 484; and for the explosion temperature (1,990°), see Muraour and Aunis, Mém. Poudres, 1932, **25**, 91. Nitroguanidine is decomposed by concentrated sulphuric acid, with a rapid evolution of nitrous oxide followed by a slower evolution of carbon dioxide and then by gases containing nitrogen. On long continued contact with water it decomposes with evolution of ammonia. When digested with ammonium hydroxide, it is converted to guanidine and urea, and with ammonium carbonate a 90% yield of guanidine carbonate may be obtained. Digestion at 60–

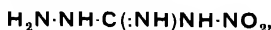
70° with methylamine gives *methylnitroguanidine*, m.p. 160.5–161°. Similarly the *ethylnitro-*, m.p. 147–148°, *butylnitro-*, m.p. 84–85° and *benzylnitro-* m.p. 183–185° derivatives may be prepared. For other alkyl nitro-derivatives, see Davis and Lucc, J. Amer. Chem. Soc. 1927, **49**, 2303. Reduction of nitroguanidine leads to the formation of, firstly, nitrosoguanidine and then aminoguanidine (*v. infra*). The reversible system nitroguanidine $\rightleftharpoons$ nitrosoguanidine has been studied by Smith and Sabetta (*ibid.* 1932, **54**, 1034) who give 0.88 as the normal oxidation-reduction potential in acid solution. The silver derivative  $\text{CH}_2\text{N}_2\text{O}_2\text{Ag}$  is colourless and almost insoluble in water, the nitrate is crystalline and melts at 147°; the hydrochloride crystallises in plates or prisms. Two qualitative tests may be used for the identification of nitroguanidine ( $\alpha$ - or  $\beta$ -). Nitroguanidine (0.01 g.) in cold water when treated with 2 drops of saturated ferrous ammonium sulphate and 1 c.c. of 6*N*-NaOH, allowed to stand 2 minutes and filtered, gives a fuchsin-coloured filtrate, fading in about half an hour. For the second test, nitroguanidine is reduced with zinc dust and 8% acetic acid and filtered. The aminoguanidine in the filtrate gives with  $\text{CuSO}_4$  solution an intensely blue solution, which, on boiling, evolves gas, and deposits metallic copper; it also reduces silver acetate in acetic acid solution. These reactions are also given by nitrosoguanidine, but the nitro- and nitroso-compounds are easily distinguished by their physical properties.

**Nitrosoguanidine**,  $\text{HN:C}(\text{NH}_2)\text{NH}\cdot\text{NO}$ , may be obtained by reduction of nitroguanidine with zinc dust and sulphuric acid or with zinc and 1–5% ammonium chloride solution (Sabetta, Himmelfarb and Smith, *ibid.* 1935, **57**, 2478). For the catalytic hydrogenation of nitroguanidine to nitrosoguanidine in the presence of Raney nickel, which may be promoted with platinum chloride, see Lieber and Smith, *ibid.* 1935, **57**, 2479; 1936, **58**, 1417, 2170. It forms yellow needles which explode violently at 161°, is soluble in alkalis and reprecipitated by carbon dioxide. 100 g. of water dissolve 0.154 g. at 20°. The isoelectric point is at  $p_H$  7. It gives the Liebermann reaction, and alkaline solutions give a beautiful purple coloration with ferrous salts (*cf.* Nitroguanidine). The estimation of nitrosoguanidine may be carried out by titration with potassium permanganate. For details of this and of other methods, see Sabetta, Himmelfarb and Smith, *loc. cit.* Aqueous solutions evolve nitrogen on boiling, but warming with concentrated hydrochloric acid gives nitric oxide (Davis and Abrams, Proc. Amer. Acad. Arts Sci. 1926, **81**, 437). A cold acidified solution converts dimethylaniline and diphenylamine into their nitroso-derivatives. The *silver salt*,  $\text{CH}_2\text{ON}_2\text{Ag}$ , is a colourless explosive precipitate; the *copper salt*,  $(\text{CH}_2\text{ON}_2)_2\text{Cu}$ , is reddish-brown and the *nickel salt*,  $(\text{CH}_2\text{ON}_2)_2\text{Ni}$ , is vermilion red (Thiele, Annalen, 1893, **273**, 133). According to Hantzsch, Schumann and Engler (Ber. 1899, **32**, 575, 1703), nitrosoguanidine is a true nitrosamine and its constitution is represented by the formula  $\text{HN:C}(\text{NH}_2)\text{NH}\cdot\text{NO}$ , since it has a neutral reaction, yields mainly nitrous acid and not nitrogen when decomposed

by acids, and does not react with phosphorus pentachloride or acetyl chloride. On the other hand, Whiteley (J.C.S. 1903, **83**, 31) and Tschugaeff (Ber. 1906, **39**, 3383) consider that the coloured metallic derivatives are salts of the tautomeric diazo-hydrate form



#### Nitroaminoguanidine,

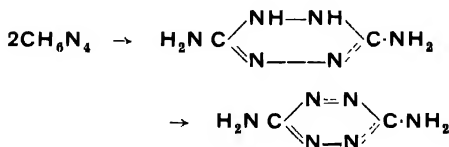


is obtained by treating nitroguanidine with hydrazine sulphate in aqueous ammonia. Its solubility in water at 20° is 0.34%, and at 70°, 3%. It melts with explosion at about 190° and reduces potassium permanganate and dichromate, Nessler's reagent, and ammoniacal  $\text{AgNO}_3$ , and with Fehling's solution yields an explosive copper compound (Phillips and Williams, J. Amer. Chem. Soc. 1928, **50**, 2465). Like other aminoguanidines and hydrazines it readily forms derivatives with aldehydes and ketones, e.g. formaldehyde nitroguanilyldrazone, m.p. 169°, and the derivative from acetone, m.p. 164–165°; acetoacetic ester, m.p. 130–131°; benzaldehyde, m.p. 188°; and salicylaldehyde, m.p. 213°. The reaction takes place rapidly in solution in water or aqueous methanol and the aldehydes or ketones may be recovered from the nitroguanilyldrazones by hydrolysis with 20% hydrochloric acid (Stoermer, Annalen, 1900, **312**, 273; Whitmore, Revukas and Smith, J. Amer. Chem. Soc. 1935, **57**, 706; Smith and Shoub, *ibid.* 1937, **59**, 2077). With nickel salts and ammonium hydroxide, nitroaminoguanidine gives  $\text{NiO}[\text{HN:C}(\text{NH}\cdot\text{NO}_2)\text{NH}\cdot\text{NH}_2]_2$  which is insoluble in water (hot or cold) but gives an intensely blue alkaline solution. This reaction may be used as a test for nitroaminoguanidine or for nickel. Reduction with zinc and acetic acid yields diaminoguanidine.

**Aminoguanidine**,  $\text{HN:C}(\text{NH}_2)\text{NH}\cdot\text{NH}_2$ , was first obtained by Thiele by reduction of nitroguanidine with zinc dust in acetic acid at 40° until a test portion developed no coloration with ferrous sulphate and alkali (Annalen, 1892, **270**, 23). After filtering and evaporating excess of  $\text{AcOH}$ , a concentrated solution of ammonium bicarbonate is added in the cold, thus precipitating the bicarbonate of the base (G.P. 59241). Modifications of Thiele's method have been described by Conard and Shriner (J. Amer. Chem. Soc. 1933, **55**, 2867) and by Wyler (U.S.P. 1990511, 2123032). A 60% yield of aminoguanidine may be obtained by the reduction of nitroguanidine with sodium in solution in liquid ammonia, provided that a sufficient concentration of ammonium chloride is maintained (Fuller, Lieber and Smith, J. Amer. Chem. Soc. 1937, **59**, 1150). A yield of 81% by electrolytic reduction, with a tin cathode, of the nitro-compound suspended in dilute sulphuric acid is claimed by Boehringer und Sohn, G.P. 167637; but this has not been confirmed (Lieber and Smith, Chem. Reviews, 1939, **25**, 216, give a detailed summary of the chemistry of aminoguanidine). The catalytic hydrogenation of the nitro-compound was suggested by McGill (U.S.P. 2033203) who used nickel on kieselguhr at temperatures between 25° and 125° in the absence of

acid, but Lieber and Smith (J. Amer. Chem. Soc. 1936, **58**, 2170) found the optimum concentration of acid is relatively high. In neutral and basic media nitrosoguanidine is the first product, but Thiele found that zinc dust and acetic acid also reduce the nitroso-compound to aminoguanidine (Annalen, 1893, **273**, 133). Aminoguanidine may also be prepared by refluxing an alcoholic solution of cyanamide and hydrazine sulphate or hydrochloride (Pollizari *et al.*, Gazzetta, 1894, **24**, i, 450; 1914, **44**, ii, 72). Previously Hoffmann and Ehrhart (Ber. 1911, **44**, 2713) had used calcium cyanamide. Improvements in this method due to Fantl and Silbermann (Annalen, 1928, **467**, 283) enable yields of 90–95% of aminoguanidine to be obtained from disodium cyanamide. Equimolecular proportions of nitrosoguanidine and hydrazine hydrate react readily, with evolution of nitrogen and water, to form aminoguanidine (Thiele, *ibid.* 1893, **273**, 133). Aminoguanidine sulphate and its  $\alpha$ -alkyl derivatives can be obtained in quantitative yield by treating S-alkylisothiourrea sulphates with hydrazine hydrate (Heyn, F.P. 618064; Schering-Kahlbaum A.-G., G.P. 463576; Smith and Anzelmi, J. Amer. Chem. Soc. 1935, **57**, 2730; Kirsten and Smith *ibid.* 1936, **58**, 800).  $\alpha\beta$ -Diaryl- $\gamma$ -aminoguanidines may be prepared from *sym*-diarylthiourreas and hydrazine hydrate in alcoholic potassium hydroxide (Busch and Bauer, Ber. 1900, **33**, 1058).

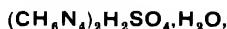
Aminoguanidine cannot be prepared in the free state; its salts when treated with an equivalent amount of barium or potassium hydroxide and evaporated *in vacuo* give reddish-violet prisms of *sym*-diaminotetrazine which results from the condensation of 2 mol. of aminoguanidine and oxidation of the diaminodihydro-tetrazine so formed:



(Thiele, *Annalen*, 1892, **270**, 1; cf. Pinner, *ibid.* 1897, **297**, 258, and Ponzio and Gastaldi, *Gazzetta*, 1913, **43**, ii, 1929; 1914, **44**, i, 257, 277). In boiling alkaline or acid solutions, aminoguanidine is hydrolysed, yielding first semicarbazido and finally ammonia, carbon dioxide and hydrazine (Thiele, *Annalen*, 1892, **270**, 1; Curtius, *Ber.* 1896, **29**, 759); if sodium carbonate is used for the hydrolysis, semicarbazide can be obtained in good yield. For the toxicity and physiological effects of aminoguanidine, see Garino, *Arch. Farm. sperim.* 1916, **22**, 229; Alles, *J. Pharmacol.* 1926, **28**, 251; Lettes, *Arch. exp. Path. Pharm.* 1924, **103**, 109; *Amer. Chem. Abstr.* 1924, **18**, 3224; *Z. ges. exp. Med.* 1924, **40**, 52; Gollwitzer-Moier, *Amer. Chem. Abstr.* 1924, **18**, 3426; and Nielsen and Widmark, *Uppsala Lakarefor.* *Forh.* 1927, [ii], **83**, 327; *Amer. Chem. Abstr.* 1929, **23**, 4973.

The determination of aminoguanidine may be made by a volumetric method which is essentially

an adaptation of the Jamieson method for hydrazine (" Volumetric Iodate Methods," The Chemical Catalog Co. Inc., New York, 1936, p. 36). The aminoguanidine salt is allowed to react with dilute sulphuric acid and a known volume of standard potassium iodate, potassium iodide is then added and the excess of oxidising agent determined with thiosulphate. Aminoguanidine forms crystalline salts with mineral acids: *aminoguanidinium chloride* forms large prisms, m.p. 163°. The *sulphate*,

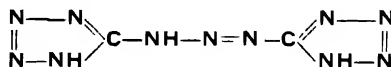


crystallises in needles, m.p. 207–208°; the *bisulphate*,  $\text{CH}_3\text{N}_4\cdot\text{H}_2\text{SO}_4$ , in large plates, m.p. 161°. With absolute sulphuric acid, aminoguanidine gives the *sulphate*  $[\text{CN}_4\text{H}_{10}](\text{HSO}_4)_4$  (Hantzsch, Ber. 1930, **63** [B], 1782). The *chloroplatinate* is yellow and insoluble, m.p. 145–146° (decomp.) (Thiele, Annalen, 1892, **270**, 1). The *picrate*,  $\text{CH}_3\text{N}_4\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , is precipitated in yellow needles from hot water. Complex salts of the type  $[(\text{CN}_4\text{H}_9)_2\text{Cu}](\text{NO}_3)_2$  are formed with copper and nickel. In the case of the copper salt, the complex is a deep violet-blue in colour and is insoluble in water (Thiele, *loc. cit.*; Smith, J.C.S. 1937, 1354). Aminoguanidine forms an addition complex with thiourea (Atkins and Werner, *ibid.* 1912, **101**, 1982) and with acid dyes it gives compounds insoluble in water (Smida, Z. physiol. Chem. 1910, **68**, 381).

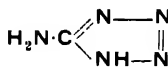
The oxidation of aminoguanidinium nitrate in dilute nitric acid with  $\text{KMnO}_4$  gives a yellow substance, azodicarbamide.



which on reduction gives the hydrazoidcarbamidine. With nitrous acid, aminoguanidine reacts in three modes, depending on the conditions of reaction. In the presence of strong mineral acid, guanyl azide ( $\text{N}_3\cdot\text{C}(\text{NH})\text{NH}_2$ ) is formed; in solution in acetic acid the product is 1:3-ditetrazolyltriazene.



which results from the intermediate production of 5-aminotetrazole,

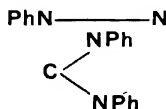


half of which is diazotised and coupled with the remainder (Hofmann and Hock, Ber. 1910, 43, 1866). If an aqueous solution of sodium nitrite and aminoguanidine nitrate is allowed to stand 6-7 days at 0-10°, the product is a white crystalline substance, 1-guanyl-4-nitrosoaminoguanylisotetrazene.



which forms readily hydrolysable salts many of which are extremely explosive. For details, see the review by Lieber and Smith (*l.c.*). Aminoguanidine and its derivatives containing the group  $\text{—NH·NH—}$ , are substituted hydrazines

and as such readily form condensation products with aldehydes and ketones. The products are usually well-characterised crystalline compounds forming crystalline salts with acids (Thiele, *Annalen*, 1892, **270**, 1; Thiele and Bihan, *ibid.* 1898, **302**, 299). For the condensation products with aldehyde, chloraldehyde and chloral, see Thiele and Dralle (*ibid.* 1898, **302**, 278); with aromatic aldehydes and ketones, see Thiele (*l.c.*), Thiele and Bihan (*l.c.*); and Wedekind (Ber. 1897, **30**, 444); with sugars, see Wolff (*ibid.* 1895, **28**, 2613); with quimones, see Thiele and Barlow (*Annalen*, 1898, **302**, 311); with a number of terpenes, see Baeyer (Ber. 1894, **27**, 1919); with pyruvic acid, see Wedekind and Bronstein (*Annalen*, 1899, **307**, 297); with glyoxylic acid, diacetyl, acetylacetone and acetylacetone, see Thiele and Dralle (*l.c.*), and Doebner and Gartner (*ibid.* 1910, **315**, 1). With  $\beta$ -diketones and  $\beta$ -ketonic esters, pyrazole and pyrazolone derivatives are formed (De and Rakshit, J. Indian Chem. Soc. 1936, **13**, 509; cf. acetylacetone) while aromatic  $\alpha$ -diketones give aminotriazines (De, Quart. J. Indian Chem. Soc. 1927, **4**, 183). Triarylamino-guanidines condense with formic acid directly or with higher aliphatic acids in the presence of phosphorus trichloride to give endomino-triazoles of which "nitron,"



has been applied to the gravimetric determination of nitric acid (Heck *et al.*, *Analyst*, 1934, **59**, 18) (*v. Vol.* II, 598c).

**Diaminoguanidine**,  $\text{HN:C(NH.NH}_2)_2$ , does not exist in the free state; the *hydrobromide* or *hydrochloride* is formed by the action of cyanogen bromide or chloride (1 mol.) on hydrazine (2 mol.) in ethereal or aqueous solution (Stollé, J. pr. Chem. 1907, [ii], **75**, 423; Stollé and Hofmann, Ber. 1904, **37**, 4524; Pellizzari and Cantoni, *Gazzetta*, 1905, **35**, i, 291; Pellizzari and Repetto, *ibid.* 1907, **37**, ii, 319; improved by Pellizzari and Gaiter, *ibid.* 1914, **44**, ii, 72). A third method of preparation is by the reduction of nitroaminoguanidine with zinc dust and acetic acid (Phillips and Williams, J. Amer. Chem. Soc. 1928, **50**, 2465). *Diaminoguanidinium bromide* crystallises in plates, m.p. 167°; the *chloride* has m.p. 185°; the *nitrate*, m.p. 143°; the *picrate*,  $\text{CH}_5\text{N}_5\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , m.p. 191°; the *platinochloride*, m.p. 172–173°. All the salts reduce Fehling's solution and ammoniacal silver nitrate solution. *Dibenzoyldiaminoguanidine*,  $\text{NH:C(NH.NH.CO.C}_6\text{H}_5)_2$ , m.p. 210–211° (Pellizzari and Cantoni, *l.c.*; Pellizzari and Gaiter, *l.c.*; Gaiter, *Gazzetta*, 1915, **45**, i, 450).

**Triaminoguanidine**,  $\text{NH}_2\cdot\text{N:C(NH.NH}_2)_2$ , does not exist in the free state; its *hydrochloride* was first obtained by Stollé (Ber. 1904, **37**, 3548) by the action of hydrazine hydrate on boiling carbon tetrachloride. It may be obtained by heating hydrazine hydrate with concentrated solutions of the salts of *guanidine*, *aminoguanidine* or *diaminoguanidine* or substances which

yield them on treatment with hydrazine hydrate, e.g. *S*-alkylisothioureas (Pellizzari and Gaiter, *l.c.*; Schotte, G.P. 501389; Amer. Chem. Abstr. 1930, **24**, 4524). Dichloroformoxime,  $\text{Cl}_2\text{C:NOH}$ , in ethereal solution reacts with an ether emulsion of hydrazine hydrate to give triaminoguanidine hydrochloride (Prandtl and Dollfus, Ber. 1932, **65** [B], 754). The *hydrochloride* has m.p. 238.5°; *thiocyanate*, m.p. 136°; *picrate*,  $\text{CH}_5\text{N}_5\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , m.p. 171°.

#### Dihydroxyguanidine Hydrobromide,

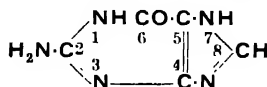


is formed by the interaction of cyanogen bromide and hydroxylamine in methyl alcohol and ether at  $-20^\circ$ ; it forms colourless needles that decompose at 95°; alkalis convert it to the deep red dihydroxy derivative,



of azodicarbamide; see *aminoguanidine*.

**GUANINE**, 2-amino-6-oxypurine,  $\text{C}_6\text{H}_6\text{O}_\text{N}_5$



was discovered by Unger in guano in 1844 (*Annalen*, 1846, **51**, 395; **58**, 18; **59**, 58), and although Hoppe-Seyler failed to find it in the excrement of fowls and geese, Haerter obtained it from the excrement of a heron (*Ardea cinerea*) fed on fish and flesh (Med. Chem. Untersuch. 1871, 582); Will and Gorup-Besanez found it in the excrement of a spider, in the organ of Bojanus of the mussel, and in the green gland of the crayfish (*cf.* Weinland, Z. Biol. 1889, **25**, 390); and Picelle found 0.0068 g. of guanine per litre in the urine of a pig fed on bran, and in an unhealthy gouty condition (*Annalen*, 1876, **183**, 141). In addition to its occurrence among the excretory products of animals, guanine is fairly widely distributed throughout the tissues; thus it is found in the liver (Smorodintzeff, Z. physiol. Chem. 1912, **80**, 231; in muscle (Bennett, J. Biol. Chem. 1912, **11**, 221); and it occurs, together with hypoxanthine, in the protamine from salmon roe, forming 6–8% of the ripe organ (Piccard, Ber. 1874, **7**, 1714); it occurs in the pancreas, spleen, liver and muscle of the ox, in quantities varying from 0.020 to 0.846% (Braginsky, Z. physiol. Chem. 1883, **8**, 395; Kossel, *ibid.* 404; Schindler, *ibid.* 1889, **13**, 432); and it is found in the skin of fishes (Ewald and Kruckenberg, Chem. Zentr. 1883, 705; see Heller, Intern. Z. Biol. 1917, **3**, 106, for possible connection between bioluminescence and guanine). Guanine is widely spread throughout the vegetable kingdom, Schützenberger found it, together with other purine bases, in yeast extract (Compt. rend. 1874, **78**, 493; Chem. Zentr. 1877, 73); Drummond and Funk in rice polishings (Biochem. J. 1914, **8**, 598). Schulze and Bosshard isolated it, together with hypoxanthine and xanthine, from young potato tubers, sugar beet, leaf buds of plane and maple, bark of plane, from lupins, red clover, vetch, young grass and oats (Z. physiol. Chem. 1884, **9**, 420). It has been found in the soya-bean

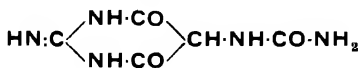
(Sasaki, J. Agric. Chem. Soc. Japan, 1932, 8, 417) and in the potato (Yoshimura, Biochem. J. 1934, 274, 408). E. von Lippmann obtained it from beet juice (Ber. 1896, 29, 2645); molasses residues boiled with copper sulphate and sodium hydroxide yield about 0.04% guanine pentoside,



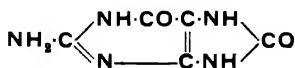
(Andrlík, Z. Zuckerind. Böhm. 1911, 35, 437). This is identical with the guanosine obtained from nucleic acid (Levene and Jacobs, Ber. 1909, 42, 2474; Biochem. Z. 1910, 28, 127); and with *vernine* (guanine-*d*-ribose),  $[\alpha]_D^{20} -8.4^\circ$  (Schulze and Trier, Z. physiol. Chem. 1911-12, 76, 145; Smolenski, Chem. Zentr. 1912, II, 709). According to Levene and Mandel (Biochem. Z. 1908, 10, 215; see also Jones and Richards, J. Biol. Chem. 1915, 20, 25), guanine is one of the cleavage products of nucleic acid, when the hydrolysis is effected by acetic acid in the presence of lead acetate at  $150^\circ$ ; cf. Levene and Jacobs (J. Biol. Chem. 1912, 12, 377); Scaffidi (Biochem. Z. 1912, 47, 215). Guanine nucleotide,  $\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_5\text{P}_2\text{H}_2\text{O}$ , has  $[\alpha]_D^{20} -13.5^\circ$  in water and  $-48.5^\circ$  in 5%  $\text{NH}_4\text{OH}$  solution (Buell and Perkins, J. Biol. Chem. 1927, 72, 21). It is found among the products of steam-heated soils (Lathrop, J. Amer. Chem. Soc. 1912, 34, 1260).

Guanine exists in guano partly as the calcium compound, partly in substances like nuclein; from these it is liberated by boiling for 4 hours with dilute sulphuric acid, the liquid is cooled and filtered, and the filtrate made alkaline with sodium hydroxide and again filtered. The guanine and uric acid are precipitated in the filtrate by the addition of ammoniacal silver solution, the precipitate washed with cold and hot water and then decomposed by hot dilute hydrochloric acid, the silver chloride filtered off, the filtrate decolorised with animal charcoal and the guanine precipitated by ammonia, a small quantity of urea in hot nitric acid is added, and the mixture set aside to crystallise. The guanine nitrate, now free from uric acid, is dissolved in dilute sodium hydroxide and the guanine precipitated by the addition of ammonium chloride, this last operation removing the xanthine (Wulff, Z. physiol. Chem. 1893, 17, 468). It may be precipitated as the phosphotungstate—for the solubility of this in a mixture of acetone and water, see Wechsler (Z. physiol. Chem. 1911, 73, 141).

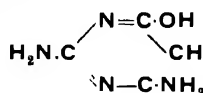
Fischer (Ber. 1897, 30, 559) has shown that guanine is 2-amino-6-oxypurine from the fact that *imino- $\psi$ -uric acid*,



obtained synthetically by Traube (Ber. 1893, 26, 2551) from guanidine and ethylmalonate, yields, on treatment with hydrochloric acid (sp.gr. 1.19), at  $120^\circ$ , the same 2-amino-6:8-dioxyurine,



as is obtained from *bromoguanine*,  $\text{C}_5\text{N}_5\text{H}_4\text{BrO}$  (Fischer and Reese, Annalen, 1883, 212, 342) by the action of hydrochloric acid at  $130^\circ$ . Further, a synthetic guanine, identical in every way with the natural product, is obtained when 6-*oxy*-2:8-dichloropurine is heated with alcoholic ammonia, and the resulting *chloroguanine* reduced by means of hydriodic acid (Fischer, Ber. 1897, 30, 2226). The synthetic production of guanine has also been effected by Traube (*ibid.* 1900, 33, 1371) from 2:4-diamino-6-hydroxypyrimidine,



obtained by the condensation of guanidine and ethyl cyanacetate in the presence of sodium ethoxide. The nitroso derivative of this compound yields, on reduction with ammonium sulphide, 2:4:5-triamino-6-hydroxypyrimidine, which, when heated with an equivalent amount of sodium formate and 8–10 times its weight of anhydrous formic acid, is converted into guanine. A similar synthetic production of guanine from 2-cyanamino-4-amino-6-hydroxypyrimidine, obtained by the condensation of dicyanodiamide and ethyl cyanacetate in the presence of sodium ethoxide, forms the subject of certain patents of Merck (G.P. 158591/1903, 162336/1904).

Guanine is an amorphous powder, insoluble in water, alcohol or ether, but soluble in acids or alkalis, forming salts of a di-acid base, or dibasic acid respectively. It can be obtained in the form of small rhombic crystals when the freshly precipitated compound is dissolved in a large excess of ammonia at  $30\text{--}35^\circ$ , and the filtered solution allowed to evaporate slowly (Drechsel, J. pr. Chem. 1881, [ii], 24, 44); or in crystals resembling those of creatinine zinc chloride, when a warm dilute alkaline solution (1:2000) is mixed with about one-third its volume of alcohol, acidified with acetic acid and allowed to cool (Horbachewski, Z. physiol. Chem. 1897, 23, 226).

The administration of guanine as food to rabbits produces neither increase in purine excretion nor pathological changes in the kidney; but subcutaneous or intravenous injections of guanine dissolved in caustic soda, causes a great increase of purine substances, especially uric acid, in the urine (Schittenhelm, Chem. Zentr. 1902, I, 1306; Schittenhelm and Bendix, Z. physiol. Chem. 1905, 43, 365; Ewald, Z. exp. Path. u. Ther. 1900, 2, 348), and diminishes the arterial blood pressure (Desgrez and Dorléans, Compt. rend. 1912, 154, 1109; Benelli, Arch. Farm. sperim. 1914, 17, 193–215); see also Desgrez and Dorléans (Compt. rend. 1913, 157, 946) for the effect of injection of guanine previous to similar injection of adrenaline.

Guanine is converted to the extent of 60–70% into xanthine when heated with excess of 25% hydrochloric acid for 32 hours (Fischer, Ber. 1910, 43, 805), and undergoes profound decomposition, yielding ammonia, carbon dioxide, formic acid and glycooll on prolonged treat-

ment with concentrated hydrochloric acid at 180–200° (Wulff, Z. physiol. Chem. 1893, 17, 468). A micro-organism belonging to the class of coccus bacteria and found in the excrement of pigeons, flourishes in a culture containing guanine, which is decomposed into urea, guanidine and carbon dioxide (Ulpiani and Cingolani, Atti. R. Accad. Lincei, 1905, [v], 14, ii, 596); it is assimilated by a number of moulds as a source of nitrogen and carbon (Kossowicz, Chem. Zentr. 1913, 1, 1297).

The following derivatives of guanine have been described:

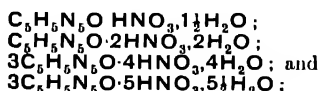
Salts.—(1) *With bases*, the sodium,



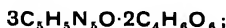
barium,  $\text{C}_5\text{H}_5\text{N}_5\text{O}\cdot\text{Ba}$ ; and copper,



derivatives. (2) *With acids*, the hydrochloride,  $\text{C}_5\text{H}_5\text{N}_5\text{O}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , forms double salts with zinc, cadmium, mercury, or platinum chloride; hydrobromide,  $\text{C}_5\text{H}_5\text{N}_5\text{O}\cdot\text{HBr}\cdot 2\frac{1}{2}\text{H}_2\text{O}$ ; hydriodide,  $\text{C}_5\text{H}_5\text{N}_5\text{O}\cdot\text{HI}\cdot 2\frac{1}{2}\text{H}_2\text{O}$ , forms a double salt with bismuth iodide; *nitrates*,



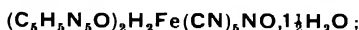
sulphate,  $(\text{C}_5\text{H}_5\text{N}_5\text{O})_2\cdot\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ ; oxalate,  $3\text{C}_5\text{H}_5\text{N}_5\text{O}\cdot 2\text{C}_2\text{H}_2\text{O}_4$ ; tartrate,



dichromate,  $\text{C}_5\text{H}_5\text{N}_5\text{O}\cdot\text{H}_2\text{Cr}_2\text{O}_7$ ; picrate,



picrolonate,  $\text{C}_5\text{H}_5\text{N}_5\text{O}\cdot 2\text{C}_{10}\text{H}_8\text{O}_6\text{N}_4$ ; ferricyanide,  $(\text{C}_5\text{H}_5\text{N}_5\text{O})_4\cdot\text{H}_3\text{Fe}(\text{CN})_6\cdot 6\text{H}_2\text{O}$ ; nitroprusside,



metaphosphate,  $\text{C}_5\text{H}_5\text{N}_5\text{O}\cdot\text{HPO}_3\cdot x\text{H}_2\text{O}$ .

(3) *Double salts*, with mercuric chloride,



silver nitrate,  $\text{C}_5\text{H}_5\text{N}_5\text{O}\cdot\text{AgNO}_3$ , the picrate of the silver salt,



is insoluble in cold water; (cf. Unger, L.c.; Strecker, Annalen, 1861, 118, 152; Balke, J. pr. Chem. 1893, [ii], 47, 539; Neubauer and Kerner, Annalen, 1857, 103, 268; Wulff, Z. physiol. Chem. 1893, 17, 468; Levene, Biochem. Z. 1907, 4, 320). *Guanine-d-glucoside*,

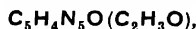


m.p. 298° (corr.) (Fischer and Helferich, Ber. 1914, 47, 210).

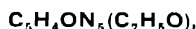
*Alkyl Derivatives*.—1. *Methylguanine* forms a heavy colourless, crystalline powder which

chars without melting (Traube and Dudley, Ber. 1913, 46, 3839). 7-*Methylguanine* crystallises in slender, colourless needles which decompose at about 390°. 1:7-*Dimethylguanine* crystallises with water of crystallisation, becomes anhydrous at 100° and melts at 343–345° (corr.); 1:7-*dimethylguanine methiodide* crystallises in large colourless plates, m.p. 330–333°. *Trimethylguanine methiodide* crystallises in colourless, slender needles, m.p. 295–300° (decomp.) (Fischer, Ber. 1897, 30, 2400; Traube and Dudley, L.c.).

*Acyl Derivatives*.—*Acetylguanine*,



is crystalline, sparingly soluble in water, alcohol or ether, and may be heated at 260° without change. *Propionylguanine*,  $\text{C}_5\text{H}_4\text{ON}_5(\text{C}_3\text{H}_5\text{O})$ , is crystalline, and remains unchanged when heated at 260°. *Benzoylguanine*,

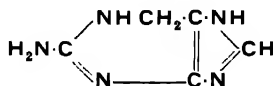


is also crystalline (Wulff, L.c.).

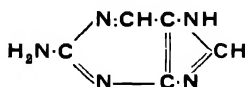
*Azo Derivatives*.—Guanine and other purine bases that are not substituted in position 7 react with diazobenzenesulphonic acid to form coloured azo compounds, in which the  $\cdot\text{N}:\text{NR}$  group is attached to carbon atom 8. Guanine and *p*-dichlorodiazobenzenesulphonic acid yield a dark red dye, which forms 8-aminoguanine when reduced. The amino compound does not itself couple with diazo compounds, but can be diazotised at 40°, and then yields a violet dye with an alkaline solution of R salt (Burian, Ber. 1904, 37, 696, 708; Hans Fischer, Z. physiol. Chem. 1909, 60, 69). This reaction has been applied by Amatore de Giacomo (Z. wiss. Mikroskop. 1910, 27, 257) to a micro-chemical method for demonstrating the presence of guanine in the renal system of birds.

*Bromoguanine*,  $\text{C}_5\text{H}_4\text{N}_5\text{OBr}$ , is a white crystalline powder, almost insoluble in water, alcohol or ether. It forms crystalline salts with acids, e.g.  $\text{C}_5\text{H}_4\text{N}_5\text{OBr}\cdot\text{HCl}$ , and also unites with lead or silver to form crystalline compounds which, when heated with methyl iodide at 100°, yield bromocaffeine. Nitrous acid converts bromoguanine into bromoxanthine (Fischer and Reese, Annalen, 1883, 221, 336).

*Deoxyguanine*,



is obtained when guanine is electrolytically reduced in 60% sulphuric acid solution; it crystallises in microscopic needles, melts and decomposes at 204° and has strongly basic properties, combining with atmospheric carbon dioxide. It is oxidised by bromine to 2-*amino-purine*,



a crystalline base more readily soluble than its isomeric, *adenine*.

**Guanine-Mononucleotide, Guanylic Acid,** has been obtained from yeast-nucleic acid as a white amorphous powder,  $[\alpha]_D^{20} -2.4^\circ$ . Its brucine salt,



has m.p.  $203^\circ$  (Read, J. Biol. Chem. 1917, **31**, 47; Jones and Read, *ibid.* 337; Foulgen, Z. physiol. Chem. 1919, **106**, 249; *ibid.* 1920, **108**, 147; *ibid.* 1920, **111**, 257). Levene has obtained the crystalline acid,  $\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_5\text{P}\cdot 2\text{H}_2\text{O}$ , from the brucine salt, this has  $[\alpha]_D^{20} -7.5^\circ$  in aqueous solution; it yields the brucine salt,



m.p.  $233^\circ$ ,  $[\alpha]_D^{20} -26.0^\circ$  in 35% alcohol (J. Biol. Chem. 1919, **40**, 171; 1920, **41**, 453).

**Tests.**—Warm dilute solutions of guanine hydrochloride give with a saturated solution of picric acid an insoluble orange-red crystalline precipitate; xanthine and hypoxanthine give a similar reaction in very concentrated solutions only (S. Capranica, Z. physiol. Chem. 1880, **4**, 233). It can be detected in animal tissue by treating it with a solution of diazobenzenesulphonic acid (sensitive to guanine) when, on addition of sodium hydroxide (after about 10 minutes), a red colour appears (de Giacomo, Z. wiss. Mikroskop, 1910, **27**, 257).

When guanine nitrate solution is evaporated it leaves a yellow residue, soluble in potassium hydroxide with a yellow coloration. On evaporating the yellow solution to dryness, it affords first a purple, then a violet coloration, and on exposure to air the original colour returns (Brücke, Monatsh. 1886, **7**, 617).

**Estimation.**—The formation of the insoluble picrate has been recommended by Wulff (Z. physiol. Chem. 1893, **17**, 468) for the estimation of guanine. See also Hoppe-Seyler and Schmidt, *ibid.* 1928, **175**, 304; Von Cordier, Monatsh. 1923, **43**, 525; Grynberg, Biochem. Z. 1932, **253**, 143; Engel, Z. physiol. Chem. 1932, **208**, 227.

**GUANO** (v. Vol. V, 63c).

**GUANOSIN DEAMIDASE** (v. Vol. IV, 315a).

**GUANOSINE** (v. this Vol., p. 89b).

**GUANYLIC ACID** (v. this Vol., p. 153a).

**GUANYLNITROSOAMINO GUANYL-TETRACENE** (v. Vol. IV, 542d).

**GUARA, Cascalotte.** The ground fruits of a variety of divi of South and Central America. The material contains 43–48% of tannins and is used as a tanning agent (Callan, J.S.C.I. 1915, **84**, 645).

**GUARANA.** Guarana is a dried paste prepared from the seeds of *Paullinia Cupana* H.B. and K., a climbing shrub inhabiting the southern and western provinces of Brazil and South Venezuela. Generally the ground or powdered seeds are moistened and kneaded into a paste, made into cylindrical or globular masses and dried before fires, in chimneys or by the heat of the sun. They are usually found in commerce in cylindrical form, 1–2 in. thick

and 5–10 in. long, with a rough, reddish-brown exterior and somewhat lighter colour inside. They have a chocolate-like odour and a bitter astringent taste. In South America guarana is an article of food used much in the same manner as we employ cocoa, and in European medicine it is administered as a nervous stimulant for the relief of certain kinds of headache. For further details as to its source, preparation and uses, see Cooke (Pharm. J. 1871, [iii], 1, 21); Hallawell (*ibid.* 1873, [iii], 3, 773); Squibb (*ibid.* 1884–1885, [iii], 15, 165); Rusby (*ibid.* 1887–1888, [iii], 18, 1050); and Marsden (Ann. Trop. Med. 1898, **4**, 105).

The physiological activity of guarana depends on the presence of caffeine (*q.v.*). Of known drugs it is the richest in caffeine. For methods of extraction, see Greene (Pharm. J. 1878, [iii], 8, 87) who extracted a mixture of guarana and 3 times its weight of litharge with boiling water; C. J. Williams (Chem. News, 1872, **26**, 97) who exhausted a moistened and slowly dried mixture of guarana and hydrate of lime with  $\text{C}_6\text{H}_6$ ; Squibb (Pharm. J. 1885, [iii], 15, 165) and Bochefontaine and Gusset (Ch. Tech. C. Anzeiger, 1886, **4**, 322) who treated a mixture of guarana and magnesia with weak alcohol and  $\text{CHCl}_3$  successively. For estimation of caffeine in guarana, see Krmel (Pharm. Post, 1888, **21**, 101). The following percentages of caffeine are selected from published analyses of guarana; 10, 5.04 (Stenhouse); 5.05 (Greene); 4.20–5.00 (5 samples, Feemster, Pharm. J. 1883, [ii], 13, 363); 4.5 (B. and Gusset); 3.12 and 3.80 (Krmel); 3.4–3.7 (Ugarte, J. Pharm. Chim. 1921, [vii], 24, 387). Thoms (Pharm. Zentralh. 1890, **31**, 533), however, states that the proportion of caffeine in guarana has been overestimated and this has been confirmed by Kirmasse (Arch. Pharm. 1898, **236**, 122), who found in 3 samples 2.68, 2.97 and 3.10%, respectively. For estimation of caffeine in guarana by an iodometric method, see Jerinstad and Ostby, Amer. Chem. Abstr. 1933, **27**, 5146. For micro-sublimation of caffeine from guarana, see Kutiaik, Amer. Chem. Abstr. 1935, **29**, 291.

Besides caffeine, guarana contains gum, starch, an acid green fixed oil, a more or less solid volatile oil, and tannin (Fournier, J. Pharm. Chim. 1861, [iii], 39, 291). The tannin further examined by Greene (Pharm. J. 1878, [iii], 8, 328) was found to behave towards reagents unlike previously known varieties, and the term *paullitanic* acid was therefore applied to it. It forms a yellowish-white amorphous mass, having an astringent taste. It is easily soluble in  $\text{H}_2\text{O}$  or  $\text{EtOH}$ . By the extraction of the crude tannin with  $\text{Et}_2\text{O}$ , crystals are obtained identical with those of the catechin of Pegu catechu (Kirmasse, *l.c.*). Krmel (*l.c.*) found 1.3–2.0% of ash consisting chiefly of phosphates.

A specimen of guarana examined by Nierenstein, probably derived from *Paullinia trigonia* Vell., was found to contain an alkaloid,  $\beta$ -guaranine,  $\text{C}_{40}\text{H}_{47}\text{O}_{21}\text{N}_4$  (?). This work was repeated by Bertrand and Carneiro (Bull. Soc. chim., 1931, [iv], 49, 1093, where references can be found), but the above results could not be confirmed.

G. B.

**GUATANNIN**, guaiacol-tanno-cinnamate (G.P. 133299).

**GUAVA** is the fruit of *Psidium guajava* L., a small tropical tree or shrub grown largely in Central and South America. The fruit is eaten raw or may be preserved, or converted into the famous guava jelly. Other subspecies of guava include:

*P. cattleianum* Ndz., the strawberry guava of Brazil having round purplish fruit;

*P. friedrichthalianum* Ndz., the yellow Costa Rican variety;

*P. molle* Bertol. or guisaro, a smaller-fruited Mexican variety; and

*P. guineense* Sw., or *P. araca* Raddi, the Brazilian guava with greenish-yellow fruit.

Thomson (Hawaii Agric. Exp. Sta. Rept. 1914, 62) gives the following analysis:

	Common guava.	Strawberry guava.
Solids . . . . .	17.32	20.72
Protein . . . . .	1.39	1.44
Fat . . . . .	0.43	0.59
Acid (as citric) . . . . .	0.51	1.23
Reducing sugars . . . . .	6.04	2.79
Sucrose . . . . .	1.28	3.91
Fibre . . . . .	4.66	6.46
Ash . . . . .	0.62	0.71

Later records by C. D. Miller (Hawaii Agric. Exp. Sta. Bull. 1937, No. 77) include the following percentage composition:

	Water	Protein	Ether extract	Crude fibre.	Carbo-hydrate.	Ash	Acid (as citric).	Ca.	P.	Fe.
Common guava, whole . . . . .	81.8	0.7	0.2	7.0	9.8	0.5	1.37	0.010	0.022	0.0015
Common guava, seed removed . . . . .	84.9	0.3	—	2.3	11.9	0.5	—	0.015	0.016	0.0003
Common guava, juice . . . . .	93.9	0.1	—	—	5.7	0.3	0.88	0.006	0.006	0.0001
Strawberry guava, whole . . . . .	81.7	0.5	0.4	6.1	10.7	0.6	1.62	0.034	0.020	0.0003

Miller and Robbins (Hawaii Agric. Exp. Sta. Rept. 1933, 25) report the vitamin C content of guava juice to be approximately half that of orange juice.

Guava seeds have the following percentage composition (Azadian, Philippine Agric. 1925, 14, 57):

Water.	Pro-tem.	Fat	Glu-Tannin	case.	Starch.	Fibre.	Ash.
10-30	15-25	14-30	1-38	0.10	13	25	42-40
							3-0

Solvent-extracted oil from the seeds is recorded by the same investigator to have the characteristics:

$d_{4}^{15}$ . . . . .	0.8243
$n_D^{40}$ . . . . .	1.4632
Saponification value . . . . .	197.1
Iodine value . . . . .	131.1
Reichert-Meissl value . . . . .	0.26
Polenske value . . . . .	0.25
Acid value . . . . .	0.55
Volatile oil . . . . .	0.25%

The following values for the seed oil from Indian-grown fruit (*Psidium guajava pyrifera*) are recorded by Varma, Godbole and Srivastava (Fettechem.-Umschau, 1936, 43, 8-9):

$d_{20}^{20}$ . . . . .	0.9365
$n_D^{25}$ . . . . .	1.4687
Saponification value . . . . .	198.7
Iodine value . . . . .	96.4
Reichert-Meissl value . . . . .	0.35
Polenske value . . . . .	0.1
Acid value . . . . .	6.4
Unsaponifiable . . . . .	0.68%

Of the fatty acids of the oil 16% are saturated (average molecular wt. 271), and the unsaturated acids (84%) include oleic 55.8, linoleic 27.8 and linolenic acid 0.4%.

**GUDMUNDITE**, Sulphantimonide of iron,  $\text{FeSbS}$ , occurring as small silver-white to steel-grey crystals embedded in calcite. The orthorhombic crystals are isomorphous with mispickel,  $\text{FeAsS}$ , and the two minerals, very similar in appearance, are associated together in lead and zinc ore at Gudmundstrop near Sala, Sweden. Analysis gave S 15.47, Sb 57.31, Fe 26.79, Ni trace, total 99.57 (K. Johansson, Z. Krist. 1928, 68, 87).

L. J. S.

**GUEJARITE** (v. Vol. II, 518a).

**GUHR** (v. Vol. IV, 239b).

**GUIGNET'S GREEN** (v. Vol. III, 107b).

**GULAMAN DAGAT**. A seaweed of the genus *Gracilaria* (Philippine Islands) furnishing agar-agar (q.v.).

**GUM BENJAMIN** (v. Vol. I, 615a).

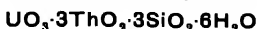
**GUM FORMATION IN COAL GAS** (v. Vol. V, 468).

**GUMMITE**. An amorphous hydrated uranium oxide ( $\text{UO}_3$  61-75%) with some lead, calcium, silica, etc. It occurs as an alteration product of *uraninite* (pitchblende), and forms yellow to reddish-brown gum-like masses, sometimes enclosing a nucleus of the unaltered parent mineral, and at times showing the external form of the original crystal. It is found together with other secondary uranium minerals at Johanngeorgenstadt, Schneeberg, and Annaberg in Saxony, in the Elias mine (*eliasite*) at Joachimsthal in Bohemia, and rather abundantly in the



Flat Rock and Deake mines in Mitchell Co., North Carolina. A gummite from Kambove, Belgian Congo, is a colloidal form of *curite* (*q.v.*) (A. Schoep, Bull. Soc. belge. Géol. 1937; 46, 309).

Related minerals are: *thorogummite*,



from Llano Co., Texas; *pylbarite*,



from Pilbara, Western Australia; and *yltrogummite*, an alteration product of *cleveite* (*q.v.*) from Norway.

L. J. S.

**GUMS.** It is almost impossible to give an accurate chemical definition of a gum. At one time the gums were considered to be carbohydrates, but it is not correct to say more than that these plant substances are closely related to the carbohydrates. The word "gum" is, in commerce, frequently applied incorrectly to a resin; for example, the so-called "varnish gums" are all true resins, and have no chemical relationship with the gums.

Most of the gums of commerce are spontaneous exudations from plants, although some may be extracted from a plant, using water as the solvent. They may be regarded as combinations of metals, principally potassium, calcium and magnesium, with complex organic acids formed by the union of various sugars or allied bodies with hexose uronic acids.

Natural gums are characterised by either being soluble in water or having the power of absorbing a large quantity of water to form a glutinous mucilage. They are precipitated from such "solutions" by comparatively small amounts of alcohol. Such mucilages, when the water is allowed to evaporate, leave the gum with considerable adhesive properties and it is this property which is generally associated with the term gum.

In the case of the better known gums, such as gum arabic, it may be taken that one end of the molecular chain consists of the residual group *d*-glucuronic or *d*-galacturonic acid, its carboxyl group being saturated by a metal. The aldehyde group of the uronic acid is joined by a glucosidic bond to an OH group of one of the sugars. A number of sugar groupings are similarly joined to the first one, and the sugars may be all alike or different. Usually at least two are present. When these bodies are hydrolysed the principal sugars obtained are galactose and arabinose. According to Butler and Cretcher (J. Amer. Chem. Soc. 1929, 51, 1519; 1930, 52, 4509) gum arabic is composed of 1 mol. of *d*-glucuronic acid, 3 mol. of *d*-galactose, 3 mol. of *l*-arabinose and 1 mol. of *l*-rhamnose.

Too much importance should not be attached to the quantitative results of any analysis of a given gum as there is no doubt that the proportions of the sugar and acid complexes, as well as the amount of the mineral matters, may vary considerably according to season, soil or climate for the gum obtained from any given species of plant.

Some gums contain as many as five different sugar complexes, and both pyranose and fura-

nose ring structures may be present. The sugars, hitherto isolated after hydrolysis of gums, are glucose, mannose, galactose, fructose, xylose, arabinose, rhamnose and fucose. For an interesting summary of the chemistry of plant gums, see Hirst and Jones (Chemistry and Industry, 1937, 56, 724).

A certain number of gums are used in pharmacy for the preparation of pastilles, emollient medicines and emulsions, their emulsifying power being very considerable. In the arts considerable amounts of several gums find employment as adhesive agents, for finishing fabrics, in calico printing, ink manufacture and the manufacture of water colours. Gum tragacanth has come considerably into fashion in the manufacture of "hair creams."

The value of most gums for commercial purposes depends on the viscosity of their solutions in water. The determination of this value is usually of a quite arbitrary character. It can, of course, be determined on standard instruments, as in the case of oils, but in actual practice it is usually done by making up solutions of a satisfactory sample, and of the sample to be tested, of the particular strength which the user employs, and allowing equal volumes of the two solutions to flow from the same tube through a narrow orifice and noting the time of flow. Although this is a "rough and ready" test, the results are extremely useful for comparative purposes.

In addition to the viscosity test, the gum must be valued by the percentages of moisture and ash, and in many cases by the acid value of the sample. Naturally, the colour, taste and odour of a solution of a gum are very important. An unpleasant odour is obviously indicative of an unsatisfactory gum, and the odour will probably be found to correspond with its acid value. For many purposes it is highly important that the solution should be of a pale colour while for other purposes colour is almost immaterial. The higher the amount of water and ash, the lower is the value of the gum. The average values for water and ash will be found under the gums described.

**Acacia Gum**, commonly known as *gum arabic*, is amongst the best known and most generally used of the true water soluble gums. It is official in the British Pharmacopoeia, which authority requires it to contain not more than 15% of moisture, nor more than 5% of ash. Its principal constituent is araban, which yields arabinose, galactose and glucuronic acid on hydrolysis. The mineral matter consists of calcium, magnesium and potassium. The most esteemed variety is that collected in Kordofan, but Mogador and Senegal gums are also of excellent quality. It is, in the main, the gummy exudation of the stem and branches of *Acacia Senegal*, although allied species also yield the gum. Artificial incisions are usually made and the bark removed. In about 2 months the first collection of gum is made. In uncultivated trees the gum exudes naturally. The gum exists in small tears, and lumps up to the size of a walnut. The fragments break with a vitreous fracture and are often quite transparent.

Apart from the question of injuring the trees

purposely, it appears that the Senegal trees yield most gum when they are in an unhealthy state, all attempts to improve their condition resulting in a smaller yield of gum.

Gum arabic is soluble in water and is precipitated by the addition of alcohol, or by basic lead acetate. The closely allied gums are of little commercial or scientific importance. An objectionable impurity in acacia gum is the so-called (*ghatti gum* which occurs in reddish tears or lumps less soluble than acacia, it is derived from various species of *Anogeissus* and the ash contains alumina and calcium phosphate.

**Gum Tragacanth.**—This gum is used in pharmacy to a considerable extent as it is a most useful emulsifier. It is also used in many other directions as a thickener, for example in thick sauces, chutneys, etc.

Tragacanth, as it is usually called, is the dried gummy exudation obtained by incision from *Astragalus gummifer* and other species. The plants are shrubs indigenous to Greece, Persia and Turkey. The exudation is collected and dried, when it forms flakes, which are graded according to their colour.

The gum is scarcely soluble in water, but swells up in contact with water to a gelatinous mass. Traces of starch are present. It is official in the British Pharmacopœia, which authority requires that it shall not yield more than 4% of ash, and shall not acquire a pink colour with a solution of ruthenium red (ammoniated ruthenium hydroxychloride) (absence of sterculia gum). The so-called Hog tragacanth is sometimes present in the lower qualities of tragacanth. This is probably the product of a species of *Prunus*. *Sterculia gum*, known as Indian tragacanth, is obtained from *Sterculia urens*. The particles are coloured bright pink by a solution of ruthenium red.

The composition of tragacanth has not been completely settled. According to Norman (Biochem. J. 1931, 25, 200), if a 0.1% "solution" be filtered, an insoluble portion, *bassorin*, remains on the filter, and a water-soluble portion, *tragacanthin*, passes through. This, on hydrolysis yields no sugar but arabinose. Norman considers tragacanthin to be a compound of arabinose and galacturonic acid only.

The early work of O'Sullivan on gum tragacanth and gum gedda laid the foundation for a good deal of the later work (J.C.S. 1884, 45, 41; 1890, 57, 59; 1901, 79, 1164). From gedda gum he isolated an acid which he termed *geddic acid*,  $C_{23}H_{38}O_{22}$ , described as an isomer of arabic acid.

According to the British Pharmaceutical Codex, 1934, the soluble portion of tragacanth yields arabinose, galactose and geddic acid, but this is not in agreement with the work of Norman above quoted.

**Bassorin**, the insoluble portion, is probably a compound of *bassoric acid* with *xylose* and possibly a sugar to which the name *tragacanthose* has been assigned. According to von Fellenberg (Chem. Zentr. 1914, II, 943) *bassorin* contains a methoxyl group. He considered that the *bassorin acid* has the formula  $C_{14}H_{20}O_{13}$ , to which the name *bassoric acid* was assigned. Other acids are stated to be present.

The numerous other gums allied to acacia and tragacanth are of little or no commercial importance. But it should be mentioned that species of *Ceratonia* yield a gum, known as *carot gum* or *locust gum*, which is an excellent substitute for gum tragacanth.

For a description of methods for identifying common gums, see Jacobs and Jaffe (Ind. Eng. Chem. [Anal.] 1931, 3, 210; cf. Wildman, J. Assoc. Off. Agric. Chem. 1935, 18, 637).

E. J. P.

**GUNARI** (v. Vol. II, 439d).

**GUN, COTTON** (v. Vol. IV, 506b).

**GURI-GINJA** (v. Vol. I, 4c).

**GURJUN BALSAM.** This oleo-resin is the product of various species of *Dipterocarpus* of which about fifty exist in South and South-East Asia. One of the most important species is *D. turbinatus*, a tree found in Bengal, Burma and the Andaman Islands. A sample of this was examined by Schimmel & Co. (Report, April, 1913, p. 68) and found to have sp.gr. 0.981 at 15°, and acid value 10.9. On steam distillation it yielded 46% of essential oil, of sp.gr. 0.927 at 15°, optical rotation  $-37^\circ$  and refractive index 1.500 at 20°. The balsam is used to some extent as an adulterant of Copaiba balsam, but in the country of its production it is sold chiefly as a varnish.

Commercial samples of the balsam have the following characteristics:

Specific gravity at 15° . . . . .	0.960–0.985
Acid value . . . . .	10–25
Ester value . . . . .	1–10

They contain from 40–55% of essential oil which has the following approximate characteristics:

Specific gravity . . . . .	0.903–0.928 at 15°
Optical rotation . . . . .	Lævorotatory up to $-130^\circ$
Refractive index . . . . .	1.500–1.5050 at 20°.

The oil consists largely of sesquiterpenes (v. GURJUNENES, THE). The presence of gurjun oil (or balsam) as an adulterant can be detected, even in quite small amounts, by the following reaction: 3 or 4 drops are added to 10 c.c. of glacial acetic acid containing five drops of nitric acid. In the presence of gurjun oil a reddish-purple to violet colour will develop within a minute.

E. J. P.

**GURJUNENES, THE.** The oleo-resins, Gurjun and Copaiba balsams, obtained from various species of *Dipterocarpus*, yield on distillation in steam an oil from which two sesquiterpenes,  $\alpha$ -gurjunene and  $\beta$ -gurjunene, have been separated (Deussen, Annalen, 1909, 369, 59; Deussen and Philipp, *ibid.* 1910, 374, 105; Semmler and Spornitz, Ber. 1914, 47, 1029; Semmler and Jakubowicz, *ibid.* 1144, 2253; Treibs, *ibid.* 1935, 68 [B], 1751).  $\alpha$ -Gurjunene has b.p. 114–116°/10 mm.,  $d_{20}^{20}$  0.919,  $n_D^{20}$  1.501,  $\alpha_D$   $-90^\circ$ , whilst  $\beta$ -gurjunene, which can be freed from  $\alpha$ -gurjunene by taking advantage of this hydrocarbon's facile oxidation with potassium permanganate, has b.p. 120–123°/13 mm.,  $d_{20}^{20}$  0.9348,  $n_D$  1.50275,  $\alpha_D$   $+74.5^\circ$ .  $\alpha$ -Gurjunene is tricyclic and gives a *monohydrochloride*, b.p. 165–170°/20 mm., from which an isomeric tricyclic hydrocarbon,  $d_{20}^{20}$  0.819,  $n_D$  1.502,  $\alpha_D$

-19°, is obtained by treatment with alkali. On hydrogenation in presence of palladium black *dihydro- $\alpha$ -gurjunene*,  $d^{20}$  0.8917,  $n_D^{20}$  1.4897,  $\alpha_D$  -18° is formed, whilst dehydrogenation with sulphur yields an azulene. By the oxidation of  $\alpha$ -gurjunene with potassium permanganate Treibs (*l.c.*) has obtained succinic acid and a tricarboxylic acid,  $C_8H_{14}O_6$ , but it is not yet possible to assign a structure to the hydrocarbon.  $\beta$ -Gurjunene, like  $\alpha$ -gurjunene, is tricyclic and gives on catalytic hydrogenation *dihydro- $\beta$ -gurjunene*, b.p. 120°/8 mm.,  $d^{20}$  0.9172,  $n_D^{20}$  1.4922,  $\alpha_D$  -42°. If repeatedly distilled over heated nickel *p*-cymene is formed (Treibs), whilst when heated under pressure at 300° for some hours it yields  $\alpha$ -terpinene (Sennler and Jakubowicz). It is not improbable that  $\beta$ -gurjunene is closely related to cedrene (*q.v.*); it gives on oxidation with chromic acid an unsaturated ketone,  $C_{15}H_{22}O$ , m.p. 43°, b.p. 163-166°/10 mm.,  $d^{20}$  1.017,  $n_D$  1.527,  $\alpha_D$  +123°, *semicarbazone*, m.p. 237°.

J. L. S.

### GUTTA PERCHA AND BALATA

are plant products containing appreciable quantities of the gutta hydrocarbon, which like the rubber hydrocarbon, caoutchouc, is a polymer of isoprene and has the formula  $(C_5H_8)_n$  or  $[-CH_2.CMe.CH_2-]_n$ . At one time gutta percha and balata were considered to contain different, although chemically related, hydrocarbons, but X-ray examination of the purified products suggests that both contain the same hydrocarbon and that it is a stereoisomer of caoutchouc.

The purified hydrocarbons of rubber, gutta percha and balata have the same general chemical properties, but the differences in spatial configuration are responsible for differences in physical properties which render the gutta and balata hydrocarbon particularly suitable for some purposes. At ordinary atmospheric temperature gutta percha and balata are much harder and less elastic than raw rubber, but soften markedly on heating and at temperatures approaching 100°C. are easily moulded, becoming hard again when cold.

Gutta percha and balata differ from each other in that they are obtained from different trees growing in different countries and are associated with different resinous materials soluble in acetone.

Gutta percha is the product obtained by coagulating the latex of certain species of *Palaquium* and *Payena* belonging to the natural order Sapotaceae which are natives of the Malay Peninsula and Archipelago. The name is derived from two Malay words "getah" and "percha" meaning plant juice of Sumatra. Balata is the product obtained by coagulating the latex of *Mimusops globosa*, a large forest tree, also belonging to the natural order Sapotaceae. This tree is a native of many countries, among which are Brazil, Venezuela and the Guianas. Whereas gutta percha is a product of the East Indies, balata is chiefly a product of the tropical region of South America.

The principal tree yielding gutta percha of good quality is *Palaquium gutta*. A number of

other species of *Palaquium* furnish gutta percha of second quality, the chief of these being *P. obovatum*, *P. maingayi* and *P. ozleyanum*. Species of *Payena* such as *P. leerii* and *P. havilandii* are also sources of gutta.

*Palaquium gutta* is a large forest tree which usually attains a height of about 60 ft. but sometimes reaches a height of 150 ft. and a diameter of 4-5 ft. The latex is contained in isolated sacs which occur chiefly in the inner layers of the bark and also in the leaves. On making incisions in the bark the latex exudes and quickly coagulates, so that only a small yield of gutta percha can be obtained at one tapping. The native method of obtaining gutta, therefore, is to fell the trees and ring them at intervals of from 9 to 12 in. The latex exudes into the incisions where it quickly coagulates and can be rolled off on a stick or removed with a knife. The amount of gutta percha obtained per tree by the native method has been variously stated, but it may be as much as 10 lb. per tree.

Owing to the serious destruction of the trees involved in the native method, attempts were made as long ago as 1845 to establish plantations and to collect the product by tapping the standing trees, but the yield was too small. Eventually mechanical methods were evolved for extracting gutta percha from leaves and twigs and a number of plantations, the chief of which is in Java, have now been established. The leaves hang on the branches for 10 to 18 months and are harvested when they are on the point of falling because they are then richest in gutta (2.6-2.7%). The average period between two picking rounds is about 40 days and the yield of gutta is about 250 lb. per acre per annum.

In order to separate the gutta percha the leaves are cut up, crushed and finally ground to a powder which is then mixed with water and allowed to ferment, after which the mixture is diluted with warm water and heated to 70°C. It is then poured into cold water when the leaf fibre sinks to the bottom and the flakes of gutta percha, being lighter than water, are easily removed. The flakes are subsequently pulverised in cold water, washed in hot water and pressed into blocks.

The crude plantation product contains about 90% gutta hydrocarbon as compared with about 80% in the best of the wild grades. A still purer grade is prepared on the plantation by extracting the crude product with cold petroleum spirit to remove resins and then dissolving the gutta in hot spirit and treating with bleaching clay to remove pigments. On cooling the gutta is precipitated as a white, snow-like mass containing less than 1% resin. The residual spirit is removed by steam distillation under a vacuum. This purified gutta readily oxidises when exposed to air and is therefore stored in evacuated tins or is treated with an antioxydant, such as *p*-toluidine, and stored in the dark or under water. This highly purified gutta is in considerable demand for the outer cover of golf balls for which purpose it is usually mixed with a little rubber during manufacture.

Like gutta percha, balata was first obtained by felling the tree, but is now obtained by

tapping, a series of incisions being made in the bark so arranged that the latex can run down to the base of the trunk where it is collected and poured into shallow dishes. This latex is remarkably stable, but on exposure to sun and air it coagulates and forms sheets which are hung to dry in the air. In some districts these sheets are pressed into blocks. Sheet balata is produced chiefly in the Guianas, and block balata in Venezuela and the Amazon districts.

The latex of balata trees usually flows freely, and, in favourable circumstances, the yield from a tree 15-20 in. diameter, tapped to a height of 8 ft., is about 3 pints, representing from 1½ to 2 lb. of dry balata.

The commercial brands of gutta percha and balata vary considerably in quality according to their origin. The quality mostly depends upon the hydrocarbon content. With the exception of the specially purified product already described, commercial material contains considerable quantities of naturally-occurring resin, as well as small quantities of foreign matter such as bark and sand. Good qualities of wild Palauquum gutta contain about 20% of resin, but balata usually contains 35-60%. For industrial purposes it is necessary to clean the commercial material by softening in hot water, washing in a masticator and straining through a fine gauze, after which it is dried by kneading and mixing under a high vacuum. For the manufacture of golf-ball covers, a solvent process, similar to that used on the gutta plantations, is employed to obtain a specially purified material.

The gutta hydrocarbon is a hard, horny, tough white substance which progressively softens on heating until at 100°C. it becomes soft and sticky, rapidly regaining its original hardness on cooling. When heated strongly in air it decomposes and burns with an odour characteristic of burning rubber. When destructively distilled it yields a mixture of hydrocarbons, including isoprene, similar to those obtained by the distillation of rubber. The gutta hydrocarbon exists in two forms, the  $\alpha$ -form being stable below about 68°C., changing to the  $\beta$ -form above that temperature. The hydrocarbon usually occurs in the  $\beta$ -form and is converted into the  $\alpha$ -form by heating at temperatures below the transition point. The  $\beta$ -form is somewhat harder and slightly more dense and more soluble than the  $\alpha$ -form. At normal atmospheric temperature the change from the metastable  $\beta$ -form to the stable  $\alpha$ -form is so slow as to be negligible, but occurs in a few hours at 60°C. (J. N. Dean, Trans. Inst. Rubber Ind. 1932, 8, 25). X-ray examination shows that gutta has a crystalline structure and that it is probably a *trans*-isomer of caoutchouc. (For a review of the subject, see Davis and Blake, "Chemistry and Technology of Rubber," Reinhold Publishing Corporation, New York, 1937, p. 120. The density of the hydrocarbon varies from 0.945 to 0.955 at 24°C. according to source and treatment.

The purified hydrocarbon is insoluble in ether, acetone, alcohol and cold petroleum spirit and is completely soluble in carbon disulphide, chloroform, carbon tetrachloride and hot petroleum spirit. In general it is soluble in

most aromatic hydrocarbon solvents, but is insoluble in saturated paraffin hydrocarbons when cold, becoming soluble on heating.

Gutta is not affected by weak mineral acids, strong hydrochloric or acetic acids, but is readily attacked by strong nitric or sulphuric acids. It is particularly resistant to hydrofluoric acid for which it is used as a container.

Gutta contains one double bond for each  $C_8H_8$  group present and forms addition products with halogens or nitrogen oxides closely resembling those prepared from rubber. Like rubber it slowly absorbs oxygen when exposed to air and light, and in the process the gutta is converted into a brittle resin. Gutta is not energetically attacked, however, by ozone, but it reacts in solution forming an ozonide which yields decomposition products similar to those from caoutchouc ozonide. The oxidation of gutta is of commercial importance since special precautions are required to prevent the deterioration of purified material. This deterioration is markedly accelerated by light and is retarded by the resins naturally occurring in the unpurified material.

Gutta is highly resistant to water, the purified material absorbing less than 0.2% over a period of 2 years.

Like rubber, gutta percha and balata can be vulcanised with sulphur and also by benzoyl peroxide and by *m*-dinitrobenzene, but the mechanical properties of the product are inferior to those of vulcanised rubber.

Analyses of commercial gutta percha and balata are necessary to assess quality, the most frequent determinations being resin, dirt and moisture. Moisture is usually estimated by heating in nitrogen at low pressure; dirt (including protein) by dissolving in benzene and filtering; and resin by extracting with hot acetone. Gutta hydrocarbon can be estimated by difference or by precipitation of the acetone-extracted material from filtered benzene solution by pouring into alcohol. The percentage composition of several representative samples of gutta percha and balata examined at the Imperial Institute or by Obach (J. Soc. Arts. 1897, 46, 125) is given in the table on the next page.

In comparison with these figures the following analysis of leaf gutta from Java is of interest, viz. gutta 79, resin 7, dirt 4, moisture 10 (Ivan Lennap, India Rubber J. 1923, 65, 367).

The resinous bodies associated with the gutta hydrocarbon in gutta percha and balata are complex oxygenated substances. They were separated by Payen in 1852 into two portions: (1) a crystalline white resin, soluble in hot but insoluble in cold alcohol, which he named *albane*; (2) an amorphous yellow resin soluble in cold alcohol, which he named *fluavile*. It is unlikely that these are pure substances and it has been shown that the resin contains appreciable quantities of  $\alpha$ - and  $\beta$ -amyrin esters (such as acetate), phytosterols such as lupeol, fats and fatty acids.

The introduction of gutta percha into commerce dates from 1843 when specimens were forwarded to London independently by two doctors resident in Singapore, William Montgomerie and José D'Almeida, and the

Variety.	Source	Gutta.	Resin.	Protein and (or) dirt.	Moisture.	Ash (included in dirt).
Geta taban merah <sup>1</sup>	<i>Palaquium gutta</i>	70.1	13.9	1.2	14.8	0.95
" " "	" "	68.3	13.4	8.1	10.2	0.89
" " putih	Uncertain	35.6	49.5	7.4	7.5	0.72
" " chaia	"	52.0	43.4	3.4	1.2	1.61
Geta Simpor	<i>Palaquium maingayi</i>	44.9	45.5	8.4	1.2	2.13
" taban Sutra <sup>2</sup>	" <i>gutta</i>	84.3	10.7	3.7	1.3	—
" sundek <sup>2</sup>	<i>Payena leerii</i>	43.9	37.6	5.1	13.4	—
Sheet balata	British Guiana	50.3	44.0	3.8	1.9	0.6
Block balata	Venezuela	45.7	44.2	8.3	1.8	1.28
Balata	Mostly British Guiana	41.5	34.8	9.9	13.8	—
"	Dutch Guiana	43.5	36.9	14.3	5.3	—

<sup>1</sup> Obtained by tapping standing trees

<sup>2</sup> Analyses by Obach

remarkable properties of the material at once attracted attention. At a meeting of the Royal Society in 1845 William Siemens suggested that it would make a suitable insulator for underground telegraph wires and in 1847 his brother Ernst Werner von Siemens employed the material for this purpose. In 1849 two experimental lengths of submarine cable insulated with gutta percha were laid at Folkestone by Walter Breit.

The first submarine cable was not a success, but many thousands of miles have now been successfully laid, nearly all of them insulated with gutta percha and a few with balata. The use of gutta percha for submarine cables is based on the ease with which it can be extruded when warm, its low water absorption, good electrical properties and the ease of effecting repairs. Submarine cables are made by warming the gutta on hot rolls and feeding it to a hot extruding machine which forces it through a die over the metal conducting core, after which the cable is passed into a tank of cold water and rolled on to drums.

The second commercial use of gutta percha in order of importance is for the outer cover of golf balls. For this purpose balata is dissolved in hot solvent and a purified gutta precipitated on cooling; this is freed from solvent and mixed with a little rubber and a white pigment on mixing rolls before moulding to the required shape. Owing to its excellent quality purified gutta supplied by the plantations has now largely replaced that previously obtained from balata.

Large quantities of balata were at one time used for the manufacture of belting, but this has been replaced to a great extent by rubber on account of cost.

Among the well-known substitutes for gutta percha for the insulation of submarine cables are Para gutta and K. gutta. They consist of mixtures of purified balata, deproteinised rubber and hydrocarbon wax or petroleum jelly.

Small quantities of gutta percha are also used as an adhesive, the best known being Chatterton's compound which is a mixture of gutta percha, Stockholm tar and resin.

G. M.

**GUTZEIT'S TEST** (v. Vol. I, 470b).

**GUVAICINE** (v. Vol. I, 458a).

**GUVAOLINE** (v. Vol. I, 458b).

**GUYACAN.** A tanning agent obtained from the seed-pods of *Carsalpinia melanocarpa* Griseb. of the Argentine.

"**GYNERGEN**" (v. Vol. IV, 330b).

"**GYNOLACTOSE**" (v. Vol. I, 242a).

"**GYNOVAL**." *isoBoryl isovalerate* ("hy-sterol"), b.p. 132–138°/12 mm. Used as a sedative.

**GYROLITE** (v. Vol. II, 227c).

**GYPSUM** (Fr. *Gypse*; Ger. *Gips*; Ital. *Gesso*). A common mineral composed of hydrated calcium sulphate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , crystallising in the monoclinic system. The name *selenite* is sometimes applied to the clear crystallised variety, *satín-spar* to the finely fibrous variety, and *alabaster* (*q.v.*) to a compact, marble-like variety used for carving. The low degree of hardness (no. 2 on the scale) is a very characteristic feature; the mineral can be readily scratched with the finger-nail. Sp.gr. 2.32. The mineral is usually white, but sometimes greyish, yellowish or reddish; and the glistening cleavage surfaces are usually conspicuous on a broken surface. The crystals possess a highly perfect cleavage in one direction parallel to the plane of symmetry; on the smooth, bright cleavage surfaces the lustre is pearly, and coloured bands (Newton's rings) are often to be seen. Cleavage flakes are flexible but not elastic (thus differing from mica), and when bent a fibrous cleavage is developed parallel to the faces of a pyramid: this fibrous cleavage is seen as silky striations on the principal cleavage, and is a very characteristic feature of gypsum.

Single crystals of gypsum, with a rhomb-shaped outline, are of common occurrence embedded in clays. Fine groups of water-clear crystals are found in the sulphur mines of Sicily, the salt mines of Bex in Switzerland and in many other localities. Enormous crystals, a yard in length, have been found in a cave in Wayne Co., Utah. Various types of twinned crystals are of common occurrence. The deposits of massive gypsum, such as are mined for economic purposes, occur as thick beds and nodular masses in sedimentary rocks of various geological periods. Those of the midlands of England are interbedded with the red marls and sandstones of Triassic age; those worked near Battle, in Sussex, belong to the later

Purbeck beds; many of the deposits of the United States are of Palæozoic (Silurian, Devonian and Carboniferous) age; whilst the important deposits in the Paris basin are of Tertiary (Eocene and Oligocene) age. These more extensive deposits of gypsum have been formed by the evaporation of water in inland lakes and seas; and they are often associated with beds of rock-salt. The mineral has, however, in many cases originated by the action of water containing sulphuric acid and soluble sulphates (produced by the weathering of iron-pyrites and other sulphides) on limestone and other calcareous rocks. It is also formed by the action of volcanic vapours on the surrounding rocks.

The output of gypsum in England amounts to about a quarter of a million tons per annum; about half of this amount is mined in Nottinghamshire, considerable quantities in Staffordshire, Sussex and Cumberland, and less in Derbyshire, Yorkshire, Westmorland and Somersetshire. The value ranges from 6 to 10 shillings per ton. In France, the output reaches  $1\frac{1}{2}$  million tons per annum, and about the same amount is produced in the United States. Nova Scotia and New Brunswick are also large producers. The French gypsum is remarkable in containing some admixed calcium carbonate and soluble silica, and for this reason it makes a harder plaster.

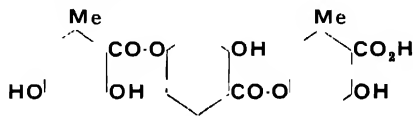
The principal use of gypsum is for the manufacture of plaster of Paris (v. Vol. II, 129-132), stucco and various kinds of wall-plasters and cements. Hence the popular name *plaster-stone*. The employment of plaster of Paris for making the moulds in the potteries has given rise to the name *potter's stone* for gypsum. In the tin-plate industry gypsum is used for polishing the plate and it is added to water to give permanent hardness in brewing. The coarser grades of material are used as fertilizers (land plaster). Alabaster

is used for carvings for inside decorations; and satin-spar is cut as beads and other small personal ornaments. Under the names "terra alba," "annaline" and "satinites," ground gypsum is used for adulterating paints, or sometimes as a legitimate constituent under specification, and as a mineral loading in the manufacture of paper (v. CALCIUM).

*References*.—R. W. Stones, "Gypsum Products, their Preparation and Uses," U.S. Bureau of Mines, 1918, Technical Paper 155; D. C. Winterbottom, "Gypsum and Plaster of Paris," Dept. of Chem. South Australia, 1917, Bull. No. 7; Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, 3, 2nd ed., 1918; "Gypsum," Imp. Min. Res. Bur. London, 1923; G. I. Adams and others, "Gypsum Deposits of the United States," Bull. U.S. Geol. Survey, 1904, No. 223; W. F. Jennison, "Report on the Gypsum Deposits of Maritime Provinces," Canada, Dept. Mines, 1911, Publ. No. 84; L. H. Cole, "The Gypsum Industry of Canada," Mines Branch, 1930, No. 714; B. Wasserstein, "Gypsum in the Union of South Africa," Bull. Dept. Mines, S. Africa, 1935, No. 3.

L. J. S.

**GYROPHORIC ACID**, occurs in *Umbilicaria pustulata* Hoffm., *Gyrophora* species and other lichens. It has m.p.  $220^{\circ}$  (decomp.). The structure of gyrophoric acid was first correctly postulated by Asahina and Watanabe (Ber. 1930, 63 [B], 3044)



and shortly afterwards confirmed by synthesis (*ibid.* 1932, 65 [B], 938; Asahina and Yoshioka, *ibid.* 1937, 70 [B], 200).

## H

**HAAS-OETTEL CELL** (Vol. III, 65d).

**HACKLING** (Vol. II, 11a).

**HÆM** (this Vol., pp. 164b, 165c).

"**HÆMAROGEN**," "**HÆMOL**." Trade names for albuminates of iron used as non-irritant assistants in the treatment of anaemia and chlorosis. These materials are frequently prepared from hæmoglobin (Massatsch, Apoth.-Ztg. 1928, 43, 1307; sterilisation, Kirilow, Problems Nutrit. (Russ.), 1936, 5, No. 3, 55) though they then differ markedly from the iron compounds prepared from albumin. The term *hæmarogen* was also applied to albuminates prepared by Bunge from egg-yolk and liver (Z. physiol. Chem. 1884, 9, 49; 1886, 10, 453).

**HÆMATIN** (this Vol., p. 164).

**HÆMATINIC ACID** (this Vol., p. 162b).

**HÆMATITE** or **HEMATITE**. A mineral consisting of ferric oxide ( $\text{Fe}_2\text{O}_3$ ), crystallising in the rhombohedral system, and an important ore of iron (Fe 70%). According to whether it is crystallised, massive, or earthy, it varies considerably in external appearance. In all

cases, however, the mineral gives a characteristic brownish-red streak or powder; and it is on account of this colour (resembling that of dried blood) that the mineral receives its name hæmatite, meaning, in Greek, blood-stone. The sp.gr. of the crystals is 5.2, but of the compact and earthy varieties it may be as low as 4.2; hardness 6 (except in the soft, earthy varieties).

The crystals are iron-black with a brilliant metallic lustre, and they vary from rhombohedral to tabular in habit. This variety is distinguished as *iron-glance*, *specular iron* or *specularite*; or, when the crystals are thin and scaly, as *micaceous iron-ore*. The compact varieties are distinguished as *red iron-ore* or *red hematite*. These sometimes exhibit a fibrous or columnar structure and a nodular surface, being then known as *kidney iron-ore*; or, when the fibrous structure is so marked that the mineral breaks into rods, as *pencil-ore*. In these cases the material is often dark-red with a dull surface, but sometimes it may be iron-black with a sub-metallic to metallic lustre. Earthy, ochreous

varieties are brighter red in colour, and are often mixed with clay and other impurities; these are known as *reddle*, *ruddle* and *red iron-froth*.

Hæmatite occurs under a variety of conditions. The best crystals are found in connection with metamorphic silicate rocks and in mineral-veins, whilst the extensive masses of red iron-ore occur as bedded deposits in sedimentary rocks, often in association with limestone. The deposits on the east coast of the island of Elba, which have been extensively worked since the time of the Romans, consist of specular iron, whilst those of west Cumberland and north Lancashire, filling large irregular cavities in limestone, consist of red iron-ore and kidney iron-ore.

Besides being used as an ore of iron, hæmatite, in its harder, compact varieties, is used, to a limited extent, as a gem-stone, and it was the material employed for some of the ancient Babylonian cylinder-seals. The pencil-ore of Cumberland is cut and polished for mounting on scarf-pins, etc., and for the burnishing tools used by jewellers and bookbinders. Ochreous varieties are used as a polishing material, and for making red paint and red pencils.

L. J. S.

#### HÆMATOGEN (Vol. II, 22a).

HÆMATOPORPHYRIN (Vol. II, 21a; this Vol., pp. 161b, 162d).

HÆMIN,  $C_{34}H_{32}O_4N_4FeCl$ . Hoppe-Seyler (Virchow's Arch. 1862, 23, 446; 1864, 29, 233) first recognised that the red pigment of the blood, for which he proposed the name hæmoglobin, consisted of a protein combined with a coloured substance, *hæmatin*. Teichmann (Z. Rat. Med. 1857, 8, 141) obtained this pigment in a crystalline state by acetic acid hydrolysis of blood. This pigment, *hæmin*, can be readily obtained from blood by a modification of Teichmann's procedure.

*Preparation*.—200 c.c. defibrinated blood is added dropwise with stirring to 1 litre 90% acetic acid containing 1 g. NaCl, at 90–95°C. After a further 15 minutes at this temperature the mixture is allowed to cool slowly. Three days later the crystals are filtered off through cloth and washed with water, alcohol and ether. 1 g. hæmin is obtained. When carried out on a micro-scale this reaction serves as a medico-legal test for blood. A small drop of blood, or a

little dried blood plus a small drop of water, and a trace of NaCl are mixed on a microscope slide and evaporated to dryness. A cover-slip is placed over the residue and a drop of glacial acetic acid run beneath it. The slide is warmed until gas bubbles appear and is then allowed to cool. The warming is repeated with a second drop of acetic acid and, when cool, the characteristic crystals of hæmin can be recognised under the microscope.

*Properties*.—Hæmin is obtained as brown or black rhombohedral needles or plates with a strong pale-blue reflex. It is insoluble in water, alcohol, ether and dilute mineral acids, but is readily soluble in pyridine, in caustic alkali and in alkali carbonates. Concentrated  $H_2SO_4$  removes iron with the formation of *prophyrin*. Hæmin sinters at 240°C. but does not melt below 300°C. (Fischer and Orth<sup>1</sup>).

#### I. CHEMISTRY OF HÆMIN AND THE PORPHYRINS.

The chemical structure of hæmin, based on the work of Hans Fischer and his school, is given in

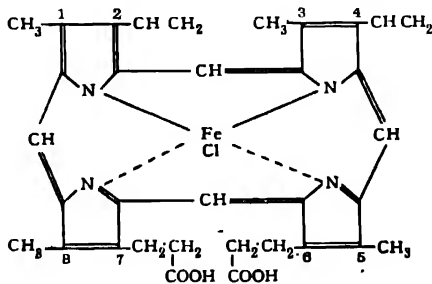


FIG. 1.

Fig. 1. Hæmin dissolves in alkali yielding a green-brown solution of *alkaline hæmatin* (—Cl replaced by —OH). When now treated with a slight excess of HCl the colour changes to red-brown and a brown precipitate of acid hæmatin is formed. In presence of a protective colloid (e.g. protein, gum arabic) the acid hæmatin remains in colloidal solution (see Section II). If hæmin is allowed to stand several days in

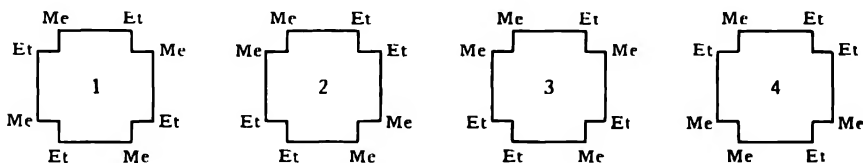


FIG. 2.

presence of an excess of glacial acetic acid saturated with HBr, the iron is removed and a purplish solution of *dibromohæmatoporphyrin hydrobromide* is obtained in which the vinyl groups are replaced by —CHBr·CH<sub>3</sub>. Crystallisation from HCl yields the hydrochloride of hæmatoporphyrin [—CH(OH)CH<sub>3</sub>] from which the free base is liberated by sodium acetate

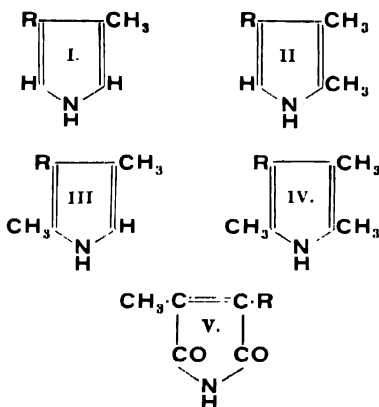
(Phummer<sup>2</sup>). On heating in a vacuum, hæmatoporphyrin loses 2 mol. of water and yields *protoporphyrin*. The term *protohæmin* is similarly used to characterise the hæmin from blood (Fig. 1) with its characteristic substituents in the pyrrole nuclei.

The chemical structure of hæmin and the porphyrins is based largely on the synthetic

work of Hans Fischer and his collaborators. The problem is greatly complicated by the large number of isomers theoretically possible by rearrangement of groups in positions 1-8 (Fig. 1). In the case of *ætioporphyrin*, where the vinyl and propionic groups are replaced by ethyl groups, there are four possibilities and the naturally occurring porphyrins and derivatives can be grouped into two of the four classes (Fig. 2). Thus, while natural protohæmin is invariably of class 3, coproporphyrin and uroporphyrin, which occur in urine and fæces, have been identified in both the 1 and 3 forms. The brown pigment of hen's egg-shell is protoporphyrin 3. Fischer has been able to synthesise all four forms of these and of many other porphyrins. The structures (class 3) of the commoner porphyrins are summarised in Table I.

The different porphyrins, as well as the four classes of each porphyrin, can be distinguished by means of their absorption spectra in acid and in alkaline solutions (Oppenheimer,<sup>3</sup> p. 400; Fischer and Orth,<sup>1</sup> Vol. II). The bile pigments (*q.v.*) are derived from the porphyrins by oxidative degradation to linear tetrapyrrolic compounds (replacement of one methine group by two  $-\text{OH}$ ).

*Degradation of Porphyrins.*—Nencki and Zaleski (Ber. 1901, **34**, 997) heated hæmin with  $\text{HI}$  in glacial acetic acid, steam distilled the residue in presence of excess of alkali and obtained an oil, "hæmopyrrole." Later workers were able to fractionate the oil into four pyrroles (I-IV,  $\text{R}=\text{Et}$ ) while from the residue were



isolated the four corresponding propionic acids ( $\text{R}=\text{CH}_2\text{CH}_2\text{COOH}$ ). Küster and Weller (Z. physiol. Chem. 1917, **99**, 253) obtained hæmatinic acid (V,  $\text{R}=\text{CH}_2\text{CH}_2\text{COOH}$ ) by oxidation with chromic acid, while a similar oxidation of mesoporphyrin yielded hæmatinic acid and methylethylmaleimide (V,  $\text{R}=\text{Et}$ ). The absence of the latter compound in the oxidation of protohæmin indicates that the unsaturated groups replace the  $\text{C}_2\text{H}_5$  groups of mesoporphyrin. Evidence of unsaturation had previously been obtained by Willstätter and M. Fischer (*ibid.* 1913, **87**, 440) who prepared an addition product with  $\text{HBr}$  which was readily hydrolysed to hæmatoporphyrin. Fischer sub-

TABLE I.

	1	2	3	4	5	6	7	8
<i>Ætioporphyrin</i>	$\text{CH}_3$	$\text{C}_2\text{H}_5$	$\text{CH}_3$	$\text{C}_2\text{H}_5$	$\text{CH}_3$	$\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5$	$\text{CH}_3$
<i>Deuterioporphyrin</i>	$\text{CH}_3$	$\text{H}$	$\text{CH}_3$	$\text{H}$	$\text{CH}_3$	$[\text{CH}_2]_2\text{COOH}$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_3$
<i>Hæmatoporphyrin</i>	$\text{CH}_3$	$\text{CH}(\text{OH})\text{CH}_3$	$\text{CH}_3$	$\text{CH}(\text{OH})\text{CH}_3$	$\text{CH}_3$	$[\text{CH}_2]_2\text{COOH}$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_3$
<i>Protoporphyrin</i> <sup>1</sup>	$\text{CH}_3$	$\text{CH}=\text{CH}_2$	$\text{CH}_3$	$\text{CH}=\text{CH}_2$	$\text{CH}_3$	$[\text{CH}_2]_2\text{COOH}$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_3$
<i>Mesoporphyrin</i>	$\text{CH}_3$	$\text{C}_2\text{H}_5$	$\text{CH}_3$	$\text{C}_2\text{H}_5$	$\text{CH}_3$	$[\text{CH}_2]_2\text{COOH}$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_3$
<i>Coproporphyrin</i> <sup>1</sup>	$\text{CH}_3$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_3$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_3$	$[\text{CH}_2]_2\text{COOH}$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_3$
<i>Uroporphyrin</i> <sup>1</sup>	$\text{CH}_2\text{COOH}$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_2\text{COOH}$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_2\text{COOH}$	$[\text{CH}_2]_2\text{COOH}$	$[\text{CH}_2]_2\text{COOH}$	$\text{CH}_2\text{COOH}$



sequently transformed hæmatoporphyrin into protoporphyrin by heating *in vacuo*.

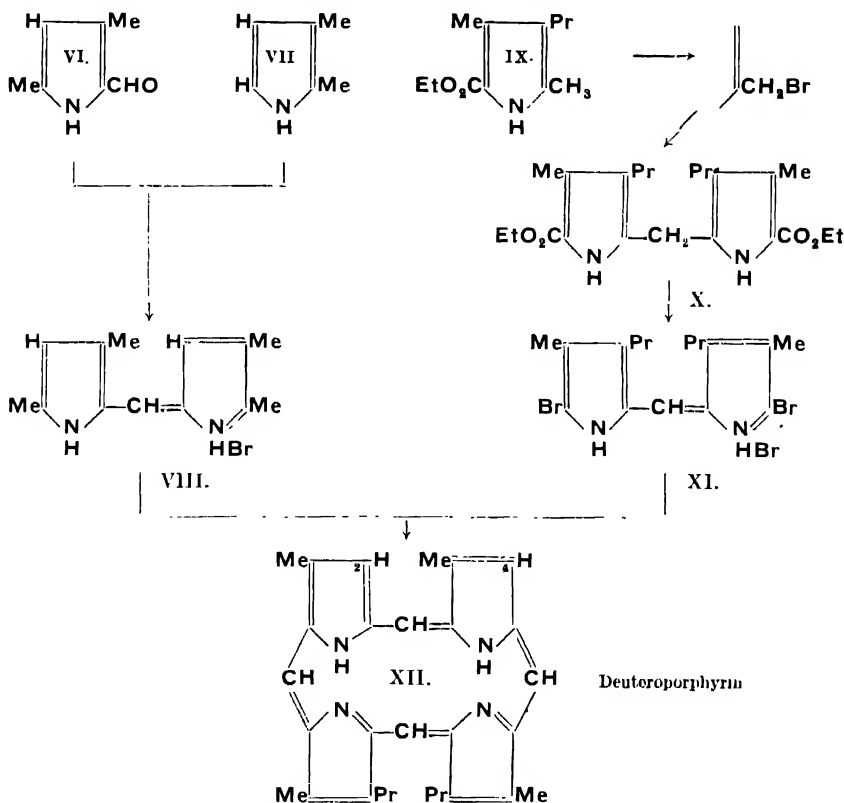
As early as 1912 Küster proposed a formula for hæmin identical with Fig. 1 except that  $\text{CH}_2$  groups occupied positions 1 and 4 while the arrangement of the four vinyl C atoms was left indeterminate. Subsequent formulae proposed by Willstätter and by Fischer were based on a tetrapyrrolethylene structure, but the present formula was established by Fischer and Stangler (Annalen, 1927, 459, 64) by synthesis of the corresponding mesoporphyrin (Fischer and Orth,<sup>1</sup> pp. 364-370).

*Synthesis of Porphyrins and of Protohæmin.*—The synthesis of hæmin *via* deuteroporphyrin is typical of the methods of porphyrin synthesis evolved by Fischer. 3:5-Dimethylpyrrole-2-al-

dehyde, VI, is condensed with 2:3-dimethylpyrrole, VII, in presence of alcoholic  $\text{HBr}$  to yield the basic component VIII. Carboxycryptopyrrolecarboxylic acid, IX

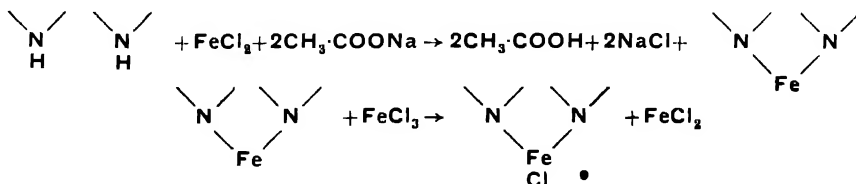


is brominated and condensed with itself ( $\text{HBr}$  in acetic acid) giving X which is hydrolysed and brominated to yield the acid component XI. By autoclaving in presence of  $\text{HBr}$ /glacial acetic acid, VIII and XI, condense to deuteroporphyrin, XII. Acetylation in positions 2 and 4 followed by reduction gives hæmatoporphyrin from which protoporphyrin is obtained by heating *in vacuo*. Treatment of protoporphyrin with ferrous chloride and sodium acetate gives rise to protohæmin



In positions 2 and 4  $\text{H} \cdot \text{CO} \cdot \text{CH}_3 \rightarrow \cdot \text{CH}(\text{OH})\text{CH}_3 \rightarrow \cdot \text{CH}:\text{CH}_2$

(Fischer, Naturwiss., 1929, 17, 611). Although reaction. In presence of air some ferric iron is the iron of protohæmin is in the trivalent state always present and the reaction proceeds as it is necessary to use a ferrous salt in the last follows:



For fuller details of porphyrin synthesis, see Fischer and Orth,<sup>1</sup> vol. II. For preparation of the intermediate compounds VI, VII and IX, see Fischer and Orth,<sup>1</sup> Vol. I.

The parent substance *porphin* with H atoms in positions 1-8 has been prepared by Fischer and Gleim (Annalen, 1935, 521, 157) by heating pyrrole- $\alpha$ -aldehyde with formic acid, and by Stern and Molvig (J. Amer. Chem. Soc. 1936, 58, 625) by condensing pyrrole and formaldehyde in methanol solution. Porphin behaves as a normal porphyrin and forms a hæmin in the usual way.

Porphyrins can be characterised not only by their absorption spectra but also by the "hydrochloric acid number." This property was defined by Willstätter as the concentration of HCl, expressed as a percentage, necessary to extract two-thirds of the porphyrin from an equal volume of ethereal solution. This principle can be applied to the fractionation of porphyrin mixtures (Zeile and Rau, Z. physiol. Chem. 1937, 250, 197). A red fluorescence in ultra-violet light at very high dilution, especially in acid solution, is characteristic of porphyrins.

Porphyrins form metallic derivatives with a large number of heavy metals in addition to iron (e.g. silver, copper, tin, aluminium, manganese,

cobalt, nickel). The iron, manganese and cobalt derivatives can be reduced to autoxidisable compounds, involving change of valency, and the ferrous derivatives combine with CO. To this class belongs the red pigment *turacin* or copper uroporphyrin which occurs in the wing feathers of the turaco (*Musophaigide*). The pigment is readily extracted by dilute alkali, and the fact that it is slowly extracted by water indicates that the pigment may be produced as a means of excreting porphyrin (Church, Proc. Roy. Soc. 1892, 51, 399; Keilin, *ibid.* 1926, B, 100, 129).

## II. REACTIONS OF HÆMATIN WITH ORGANIC BASES AND PROTEINS.

The reaction between hæmatin and organic bases is of particular interest as the resulting compounds may serve as spectroscopic models of the natural hæm-protein catalysts (e.g. hæmoglobin), and also provide a simple means of estimation of hæmatin in tissues by spectroscopic comparison with standard solutions of hæmin. Fig. 3 summarises the inter-relationships of these compounds and their relationship to hæmoglobin. For further details, see Keilin (*l.c.*).

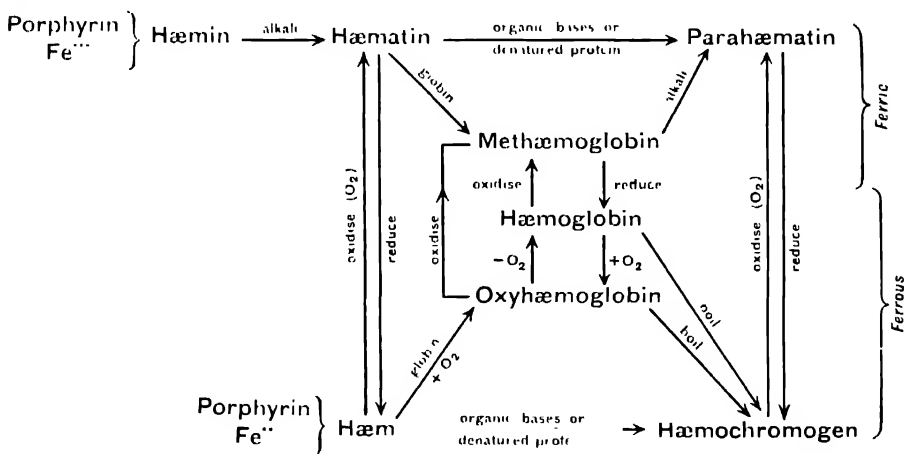


FIG. 3.

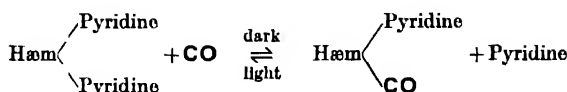
When treated with pyridine (or other organic bases) hæmatin forms an addition product *parahæmatin*. The solution becomes greener, but the diffuse absorption spectrum is not greatly changed. However, if the solution is now reduced ( $\text{Na}_2\text{S}_2\text{O}_4$ ), the colour changes to pale red and the resulting *hæmochromogen* has two sharp absorption bands at 5590Å. and 5257Å.; the former being more intense. Hill and Holden (Biochem. J. 1926, 20, 1326) and later Anson and Mirsky (J. Gen. Physiol. 1930, 13, 469) succeeded in separating the protein of hæmoglobin, or *globin*, from the hæmatin without denaturing the former. By adding this globin to an alkaline solution of protohæmin, *methæmoglobin* was obtained (see Section VI) which was reduced to hæmoglobin. Globin has also been added to a number of other hæmins, and of the resulting

artificial hæmoglobins some exhibited the characteristic property of oxygenation. Methæmoglobin may be prepared directly from oxyhæmoglobin by oxidation of the ferrous iron with  $\text{K}_3\text{Fe}(\text{CN})_6$ . During this reaction the combined oxygen of oxyhæmoglobin is liberated and the distinction between oxidation and oxygenation is clearly demonstrated.

If the mild procedures described by the above authors are not followed the protein becomes denatured, and a parahæmatin or hæmochromogen is formed according to the valency of the iron. Thus if blood is boiled, the hæmochromogen spectrum appears; if treated with alkali and dialysed against water, parahæmatin is formed.

All the ferrous compounds of Fig. 3 combine reversibly with CO, the absorption spectrum changing in each case. With hæm and hæmo-

chromogens the reaction is reversed by light and the following reaction takes place with reduced hæmatin (hæm) and pyridine in presence of CO.



abs bands 5762A., 5385A.

In absence of CO, hæm and hæmochromogen are autoxidisable.

### III. OCCURRENCE IN NATURE.

Hæmatin is present in all animal and vegetable tissues, in yeast and aerobic bacteria, and is an essential constituent of all aerobic cells where it occurs either in the free state or, more usually, as hæm-protein complexes functioning as respiratory catalysts, examples of which are described in this article. The concentration of hæmatin is greatest in tissues of high respiratory activity, or in a region where growth is very rapid. This is particularly noticeable in the case of the hæm-protein *cytochrome* (*q.v.*; see also Keilin, Proc. Roy. Soc. 1925, B, 98, 312). Crude oils and bituminous minerals contain considerable quantities of hæmatin derivatives which can be observed with a direct-vision spectroscope. Most of these porphyrins are derived from chlorophyll but a small proportion of mesohæmatin, a reduction product of protohæmatin, can be detected. The porphyrins are present as metal derivatives; apart from iron, vanadium is commonly found (Treibs, Annalen, 1934, 510, 42; 1935, 517, 172).

### IV. ESTIMATION.

The detection and estimation of free and combined hæmatin is most readily carried out by conversion to hæmochromogen (pyridine and  $\text{Na}_2\text{S}_2\text{O}_4$ ) which, of all hæmatin derivatives, has the most intense absorption spectrum (*see* Section II). The most convenient instrument to use is a Zeiss microspectroscope which has the necessary small dispersion and is fitted with a comparison prism to allow comparison of two spectra side by side. The solution or tissue extract to be examined is treated with alkali, to dissociate protein from hæmatin, followed by pyridine and  $\text{Na}_2\text{S}_2\text{O}_4$ . The absorption bands of hæmochromogen can be observed in a 2 cm. depth of fluid containing only 0.001 mg. hæmin per c.c.

The concentration of hæmatin can be determined to within 2–3% by comparing the spectrum with that of a variable depth of a standard solution of hæmin crystals in sodium hydroxide similarly treated with pyridine and  $\text{Na}_2\text{S}_2\text{O}_4$  (Hill, Proc. Roy. Soc. 1929, B, 105, 112). The small dispersion of the Zeiss instrument permits accurate measurements with cloudy solutions. By the same method Elliot and Keilin (*ibid.* 1934, 114, 210) were able to estimate hæmatin in intact vegetable tissue. A cube of the material (*e.g.* horse-radish root) was treated with pyridine and  $\text{Na}_2\text{S}_2\text{O}_4$  in a vacuum when the root became sufficiently trans-

lucent for comparison of spectra. By this method the distribution of hæmatin in the entire cross-section of a plant can be rapidly determined.

The position of the absorption bands is determined by the chemical structure of the hæmatin nucleus rather than by the nitrogenous substance with which it is combined.

### V. HÆMOGLOBIN AND MYOGLOBIN.

**Hæmoglobin** (*v. BLOOD*).—This respiratory pigment is present in the blood of all vertebrates and is also distributed in a haphazard manner among the invertebrates where the oxygen supply is intermittent or irregular (*e.g.* *Arenicola*, *Lumbricus*, *Planorbis*, *Chironomus*; see M. Florkin, "Transporteurs d'oxygène," Paris, 1934). Hæmoglobin is an intracorporeal pigment in vertebrates but is in solution in invertebrate blood.

The hæmoglobin molecule consists of 4 mol. of hæm (reduced protohæmatin) and 1 of globin (*see* Section II). It is a purplish-red pigment which combines reversibly with oxygen to give bright red oxyhæmoglobin, the equilibrium between the two forms being determined by the oxygen tension. The chemistry of the phenomenon of oxygenation has been investigated by a number of workers (Anson and Mirsky, J. Physiol. 1925, 60, 165; Barnard, Proc. Soc. Exp. Biol. Med. 1932, 30, 43; see J. Barcroft <sup>4</sup>) and its biological significance is discussed below.

Hill and Holden (*see* Section II) were able to examine the reaction between undenatured globin from hæmoglobin and various porphyrins and metallo-porphyrins (Biochem. J. 1926, 20, 1326). They obtained spectroscopic evidence that native globin will combine with proto-, hæmato- and meso-porphyrins (with a marked change in colour) as well as with iron derivatives of each. No evidence could be obtained that denatured globin or other proteins would react with the free porphyrins. Haurowitz and Waelsch (Z. physiol. Chem. 1929, 182, 82) discuss the mode of combination of protohæmatin and globin. They consider that the vinyl and carboxyl groups can play no part in the reaction, owing to the existence of artificial hæmoglobins in which these groups are absent, and that the pyrrole N-atoms are too inert. They regard the reaction as complex-salt formation involving only the Fe atom and point out the similarity in behaviour of hæmoglobin and inorganic complex salts towards acids, alkalis and organic bases. While this hypothesis may well hold for hæmochromogens, the work of Hill and Holden as well as that of Warburg and Negelein (Biochem. Z. 1932, 244, 9) does indicate that globin may also

be attached to other points of the hæmatin molecule. These latter authors measured the  $O_2$  capacity of a number of artificial hæmoglobins and found that it varied between 0 and 72% of the theoretical value, with varying substituents in the hæmatin nucleus. The nature of the Fe-protein linkage has also been considered by Hill (*ibid.* 1925, 19, 341).

Oxyhæmoglobin may be purified by crystallisation. The tendency to crystallise and the crystalline form vary considerably with the species (Abderhalden,<sup>2</sup> p. 185; Hawk and Bergheim<sup>3</sup>) while the positions of the absorption bands vary slightly among vertebrate oxyhæmoglobins although invertebrate oxyhæmoglobins show larger variations. The average positions of the bands of vertebrate oxyhæmoglobins are  $\alpha$ -5770 $\text{\AA}$ . and  $\beta$ -5240 $\text{\AA}$ ., the former being more intense. The spectrum of reduced or deoxygenated hæmoglobin is very diffuse. If the  $O_2$  of oxyhæmoglobin is replaced by CO the absorption maxima move slightly towards the blue as indicated in Table II (Anson, Barcroft, Mirsky and Oinuma, Proc. Roy. Soc. 1924, B, 97, 61). If A and B are the positions in Angstrom Units of the  $\alpha$ -bands of  $O_2\text{Hb}$  and  $\text{COHb}$  and  $K$  is the equilibrium constant of the reaction  $\text{CO} + O_2\text{Hb} \rightleftharpoons \text{COHb} + O_2$  then, according to these authors,  $\log K = 0.05(A-B)$ .

TABLE II.

Animal	Position of $\alpha$ -band in Angstrom Units.	
	$O_2\text{Hb}$	$\text{COHb}$
Man . . .	5,764	5,710
<i>Arenicola</i> . .	5,746	5,698
<i>Lumbricus</i> . .	5,755	5,720
<i>Planorbis</i> . .	5,746	5,708
<i>Chironomus</i> . .	5,777	5,727
Pigeon . . .	5,762	5,710
Carp . . .	5,762	5,716
Horse . . .	5,764	5,708
Tortoise . . .	5,766	5,717
Fowl . . .	5,769	5,718
Lizard . . .	5,762	5,715

(Hb=hæmoglobin.)

Accurate measurements of wave-length are most conveniently carried out with the Hartbridge reversion spectroscope (J. Physiol. 1922, 57, 47).

Analyses of the amino-acids constituting globins from various sources have been recorded by J. Roche, "Biochimie générale et comparée des pigments respiratoires," Paris, 1936.

Crystalline oxyhæmoglobin is readily prepared by the following method (Keilin and Hartree, Proc. Roy. Soc. 1935, B, 117, 1): 600 c.c. fresh defibrinated horse-blood is centrifuged and the serum removed. The corpuscles are washed 3 times, by centrifuging, with 0.9% NaCl. 300 c.c. washed corpuscles are cooled to 0°C., shaken for  $\frac{1}{2}$  minute with 90 c.c. cold water and 90 c.c. cold pure ether and centrifuged. The lower clear layer is dialysed for 24 hours at 0°C. against distilled water and treated drop by drop

with cold absolute alcohol until the solution contains 20% alcohol. Oxyhæmoglobin slowly crystallises out at 0°C. and can be recrystallised several times as follows: the cake of crystals is suspended in an equal volume of water, warmed to 37°C. and treated with the minimum of  $N\text{-NaOH}$  for complete solution. The solution is cooled, treated cautiously with  $N\text{-HCl}$  equivalent to the  $\text{NaOH}$  used, centrifuged to remove impurities and set aside at 0° to crystallise. During recrystallisations the pigment becomes progressively less soluble in water. It is obtained as slender needles up to 2 mm. in length.

The determination of the molecular weight of hæmoglobin has been recorded in a previous article (*see* BLOOD) and a value of 68,000 is now accepted for vertebrate hæmoglobin. The molecular size of invertebrate hæmoglobins varies considerably.

The estimation of oxyhæmoglobin can be carried out spectrophotometrically if other pigments are absent, but the most reliable method the measurement of the oxygen capacity. The hæmoglobin molecule, containing 4 hæmatin groups, takes up in air 4 mol. of oxygen. As already described (Section II) oxyhæmoglobin gives up its oxygen when oxidised to methæmoglobin, and it is only necessary to add an excess of  $K_3\text{Fe}(\text{CN})_6$  to a known volume of oxyhæmoglobin solution in a suitable manometric apparatus. For this purpose the manometers of Barcroft or Warburg are most suitable (*see* M. Dixon, "Manometric Methods," Cambridge, 1934). Thus, if 3 c.c.  $O_2\text{Hb}$  solution evolves  $v$  cu.mm.  $O_2$  at N.T.P. on oxidation, then, as 68,000 g.  $O_2\text{Hb}$  would combine with  $4 \times 22.4$  l. the weight of  $O_2\text{Hb}$  in 3 c.c. solution is

$$\frac{v \times 68,000}{4 \times 22.4 \times 10^6} \text{ g.}$$

**Myoglobin.**—When blood is completely removed from an animal by perfusion it will be found, on spectroscopic examination of thin slices of various organs, that a red pigment very similar to hæmoglobin is often present, and that its concentration is greatest in tissues of high respiratory activity. If a perfused heart is finely minced, extracted with 0.9% NaCl and the extract clarified with kieselguhr, a solution of this pigment, known as *muscular hæmoglobin* or *myoglobin* is obtained. The pigment combines reversibly with  $O_2$  (when the absorption maxima (horse-heart) are  $\alpha$ -5815 $\text{\AA}$ .,  $\beta$ -5446 $\text{\AA}$ .), and also with CO. The pigment forms a metmyoglobin and in its general properties is very similar to hæmoglobin. The pigment has been obtained in a crystalline state by Theorell, who has studied the spectroscopy of its derivatives, its reactions with  $O_2$  and CO, and found the molecular weight, by ultracentrifugal methods, to be 34,000; the molecule containing 2 mol. of protohæmatin (Biochem. Z. 1932, 252, 1; 1934, 268, 46). As a result of more recent measurements, a value of 17,000 is now accepted (Svedberg<sup>7</sup>). Hill has suggested (Proc. Roy. Soc. 1936, B, 120, 472) that "muscle hæmoglobin indicates a presence of a reserve of oxygen not only in cases of intermittent supply but also in cases of intermittent consumption of oxygen." Millikan (*ibid.* 1936, [B], 120, 366; 1937, [B],

123, 218) using an apparatus in which reaction velocities could be measured by spectrum changes over very small intervals of time ( $<10^{-3}$  sec.) showed that  $O_2$  combines more rapidly with myoglobin than with hæmoglobin. This author calculates that the oxygen stored by myoglobin in mammalian heart suffices for 10–15 seconds at rest or 2–3 seconds at high activity. This store could, therefore, tide the heart-muscle over from one contraction to the next. The oxidation of myoglobin (as distinct from its oxygenation) by molecular oxygen is also more rapid than that of hæmoglobin.

*Kinetics of Hæmoglobin and Myoglobin.*—Myoglobin was found by Hill (*l.c.*) to possess a higher affinity for oxygen than hæmoglobin and the relationship is summarised in Fig. 4 (reproduced by permission of the author). This figure

indicates the percentage of each pigment in the oxygenated form under various pressures of oxygen. Whereas the pressure of oxygen in the venous blood of man is 40 mm. Hg, the oxidase activity of the cell functions most efficiently at a lower pressure (*e.g.* 5 mm. Hg). At the former pressure myoglobin is 94% saturated and at the latter pressure 80% saturated with  $O_2$ . Myoglobin can thus act as an efficient oxygen carrier between the circulatory hæmoglobin and the enzyme system of the cell. Hill has calculated that the oxygen made available from myoglobin by a drop in oxygen pressure from 40 mm. to 5 mm. would, in mammalian heart muscle, supply sufficient oxygen for 1 second's normal consumption, *i.e.* for approximately the duration of 1 heart beat.

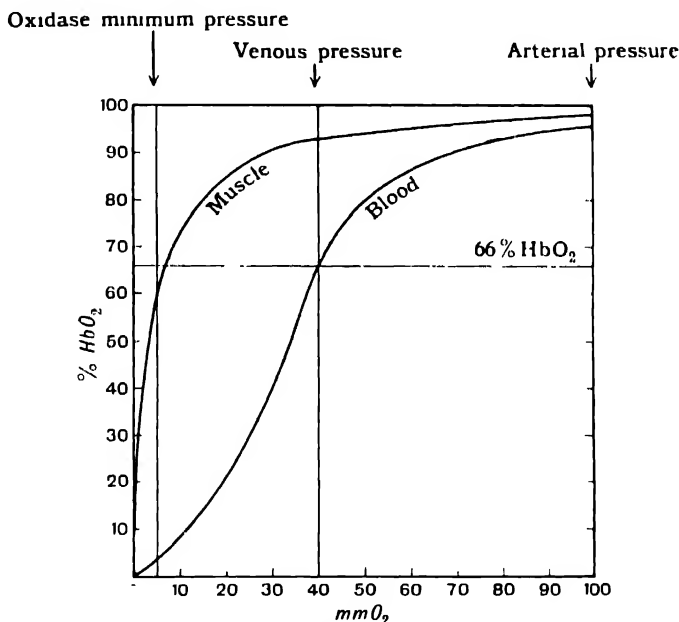


Fig. 4.

The relative affinities of these pigments for  $O_2$  and CO is expressed by

$$K = \frac{[HbCO] \cdot [O_2]}{[HbO_2] \cdot [CO]}$$

Hæmoglobin has a much higher affinity for CO than for  $O_2$  and values of  $K$  between 100 and 600 have been found for various hæmoglobins (Anson, Barcroft, Mirsky and Oinuma, *Proc. Roy. Soc.* 1924, B, 97, 61). The value of  $K$  for myoglobin is much lower; Theorell (*Biochem. Z.* 1934, 268, 64) finding values of the order of 20 for horse myoglobin.

#### VI. METHÆMOGLOBIN, PEROXIDASE AND CATALASE.

**Methæmoglobin.**—As previously mentioned, hæmoglobin can be oxidised to methæmoglobin,

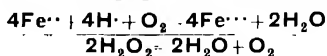
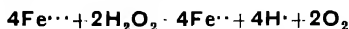
the corresponding ferric compound, by means of  $K_3Fe(CN)_6$  (*see* Keilin and Hartree, *Proc. Roy. Soc.* 1935, B, 117, 1). Below  $p_H$  7 a brown solution of acid methæmoglobin is obtained with absorption bands at 5040Å., 5475Å., 5820Å. and 6370Å. The last band is most prominent in visual observations. The spectrum is far less intense than that of oxyhæmoglobin, and a low-dispersion spectroscope is essential. Above  $p_H$  8 alkaline methæmoglobin is formed which is more reddish and has absorption maxima at 5750Å. and 5450Å. Methæmoglobin does not combine with CO or  $O_2$  but forms a series of spectroscopically well-defined compounds with the respiratory inhibitors HCN,  $HN_3$ ,  $H_2S$ , HF,  $NO$ ,  $H_2O_2$ , and organic peroxides (*e.g.*  $C_2H_5OOH$ ). In this respect methæmoglobin is closely analogous to the respiratory catalysts, peroxidase and catalase. The study of the

formation of a definite compound between methæmoglobin and  $\text{H}_2\text{O}_2$  (Keilin and Hartree, *l.c.*) led to the elucidation of the mechanism of the biologically fundamental reactions of peroxidase and catalase with  $\text{H}_2\text{O}_2$ .

**Peroxidase.**—This enzyme is very widely distributed in vegetable tissues but appears to be absent from animal tissues (except milk). It is a protohæmatin-protein complex which has not yet been obtained in a pure state. It is obtainable most readily from horse-radish root and it catalyses the oxidation by  $\text{H}_2\text{O}_2$  of many phenols and aromatic diamines (e.g. pyrogallol, hydroquinone, *p*-phenylenediamine), as well as of ascorbic acid (Willstätter and Pollinger, *Annalen*, 1923, **430**, 269; Kuhn, Hand and Florkin, *Z. physiol. Chem.* 1931, **201**, 255). Elliot and Keilin (*Proc. Roy. Soc.* 1934, **B**, **114**, 210) demonstrated an approximate proportionality between hæmatin content and peroxidase activity during purification, while Keilin and Mann (*ibid.* 1937, **B**, **122**, 119) were able to show that the activity was strictly proportional to the the spectrum intensity. The spectrum is very similar to that of methæmoglobin with bands at 4980Å., 5480Å., 5830Å., 6450Å. The latter authors recorded compound formation with the above inhibitors and the compound with  $\text{H}_2\text{O}_2$  was the first example of an enzyme-substrate compound. Such compounds had always been postulated in studies of the mechanism of enzyme action. The same authors' purest preparation contained 1.5% hæmatin and may be considered as 40% pure on the assumption that peroxidase will contain the same proportion of hæmatin as methæmoglobin (i.e. 3.8%). Hæmatin and all hæmatin derivatives possess a slight peroxidatic action and this fact has led to the reporting of heat-stable animal peroxidases. In such cases, the activity per milligram hæmatin is incomparably smaller than that of peroxidase which, like other hæm-protein enzymes, is destroyed by heating to 70°C.

**Catalase** (*see also* CATALASE).—The occurrence of this enzyme, which decomposes  $\text{H}_2\text{O}_2$  into molecular oxygen and water, is almost entirely restricted to animal tissues where it is very widely distributed. Considerable quantities occur in blood and liver. Like peroxidase it is a protohæmatin-protein complex with a 4-banded spectrum: 5065Å., 5440Å., 5800Å., 6295Å. (Euler and Josephson, *Annalen*, 1927, **452**, 158; Zeile and Hellström, *Z. physiol. Chem.* 1930, **192**, 171). Keilin and Hartree (*Proc. Roy. Soc.* 1936, **B**, **121**, 173) described a simple method of preparation from horse liver and demonstrated a strict proportionality between the intensity of the catalase absorption spectrum and the hæmatin content of a series of catalases from horse liver, and later (unpublished results) found a similar proportionality between hæmatin content and catalase activity. The preparation of crystalline catalase from ox-liver (Sumner and Dounce, *J. Biol. Chem.* 1937, **121**, 417) and the measurement of its sedimentation velocity in the ultra-centrifuge (Stern and Wyckoff, *Science*, 1938, **87**, 18) showed that the molecular weight of catalase is of the order of 270,000 and four hæmatin molecules occur per molecule. Recent work (Lemberg, Norrie and Legge, *Nature*, 1939,

144, 551) has cast some doubt on the equivalence of the four hæmatin nuclei and indicates that only three are protohæmatin. Catalase, like methæmoglobin, forms a series of compounds with the respiratory inhibitors (Keilin and Hartree, *l.c.*), while the mechanism of the decomposition of  $\text{H}_2\text{O}_2$  into water and molecular oxygen has been explained by the same authors (*Proc. Roy. Soc.* 1938, **B**, **124**, 397) as a reduction of  $\text{Fe}^{+++}$  of catalase by  $\text{H}_2\text{O}_2$  followed by its re-oxidation by oxygen.



## VII. OTHER NATURALLY-OCCURRING HÆMATIN DERIVATIVES.

### Cytochrome (*q.v.*).

**Chlorocruorin.**—Ray Lankaster (*J. Anat. Physiol.* 1867, **2**, 114) gave the name chlorocruorin to the red hæm-protein pigment dissolved in the plasma of certain polychæte worms. It acts as an oxygen carrier and its spectra in the oxygenated and deoxygenated forms are similar to those of hæmoglobin, though the bands are nearer to the red end of the spectrum.

The hæmin was isolated and examined by Fox (*Proc. Roy. Soc.* 1926, **B**, **99**, 199) while, according to Fischer and von Seemann (*Z. physiol. Chem.* 1936, **242**, 133), it is identical with the so-called *spirographishæmin*, i.e. as Fig. 1 with —CHO replacing —CH:CH<sub>2</sub> in position 2.

**Helicorubin.**—A hæmochromogen occurring in the gut of snails, especially in *Helix pomatia* during hibernation. Its function is unknown (Dhéré and Vegezzi, *J. Physiol. Path. gén.* 1917, **17**, 44).

## VIII. BIBLIOGRAPHY.

Publications are referred to in the text under the authors' names.

1. H. Fischer and H. Orth, "Die Chemie des Pyrrols." 2 vols., Leipzig, 1934, 1937.
2. E. Abderhalden, "Handbuch der Biologischen Arbeitsmethoden," Abt. I, Teil 8, Berlin, 1922, containing articles by Schultz (Darstellung von Blutfarbstoffen) and by Küster on hæmatin and porphyrins.
3. C. Oppenheimer, "Handbuch der Biochemie," 2 Aufl., Band I, Jena, 1924, containing articles by Muller and Biehler (Respiratorische Farbstoffe) and by Fischer (Farbstoffe mit Pyrrolkernen).
4. J. Barcroft, "The Respiratory Function of the Blood," Part II, Cambridge, 1928.
5. R. H. A. Plimmer, "Organic and Biochemistry," London, 1938.
6. P. B. Hawk and O. Bergheim, "Practical Physiological Chemistry," London, 1938.
7. T. Svedberg and others, "A discussion on the protein molecule," *Proc. Roy. Soc.* 1939, **B**, **127**, 1.

E. F. H.

**HÆMOCHROMOGEN** (this Vol., p. 164b).

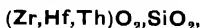
**HÆMOGLOBIN** (Vol. II, 20; this Vol., p. 165c).

**HÆMOPYRROLE** (this Vol., p. 162a).

**HAFNIUM.** Hf. At. no. 72, at. wt. 178.6.

In 1923 D. Coster and G. von Hevesy detected in the X-ray spectra of a number of zirconium minerals six lines attributable to an element 72. They asserted that two of these lines were not identical with two lines observed by Dauvillier in 1922 in certain rare earths, and hence could not be identified with a new element "celtium" which had been claimed by Urbain to be present in the same rare-earth preparation. Coster and Von Hevesy proposed the name *hafnium* (from Hafnia, an old designation for Copenhagen) for element 72, and showed that it could be separated chemically with zirconium from any accompanying rare earths, and that it did not yield the optical spectra assigned by Urbain to "celtium" (Nature, 1923, 111, 79, 182, 252, 462).

All zirconium minerals contain hafnium, although in greatly varying amounts; the oxides contain 1-2%, the silicates such as zircon 2-6%. *Albite*, a complex orthosilicate,



from Kragerø, Norway, contains 34% of zirconia and 16% of hafnia. The zirconium extracted from the complex minerals *euxenite* and *fergusonite* contains from 5 to 6% of hafnium. *Thortveitite*, from Madagascar, contains 3.2%  $\text{HfO}_2$  and 2%  $\text{ZrO}_2$ . Hafnium is as abundant in the earth's crust as thorium and about one-tenth as plentiful as zirconium.

**Separation from Zirconium.**—Hafnium exhibits a close chemical similarity to zirconium, and they remain associated when the latter is separated by the usual methods from the rare earths and thorium. Materials containing hafnium and zirconium are fused with potassium hydrogen fluoride and the double fluorides  $\text{K}_2\text{XF}_6$  ( $\text{X} = \text{Hf}$  or  $\text{Zr}$ ) are separated by fractional crystallisation in aqueous solution. The hafnium salt is more soluble and in this way a product of 99.9% purity is obtainable. A convenient alternative consists in the fractionation of the ammonium double fluorides, that of hafnium being the more soluble.

Hafnium ammonium sulphate is also more soluble than the corresponding zirconium double salt and may be used in these separations.

The phosphates  $\text{XO}(\text{H}_2\text{PO}_4)_2$  also serve for this separation, the hafnium phosphate being appreciably less soluble in concentrated acids than the zirconium compound. The freshly precipitated mixed phosphate dissolves in oxalic acid and on adding hydrochloric or sulphuric acid is reprecipitated in a readily filterable form. In this process hafnium accumulates in the less instead of in the more soluble fractions. This method is available on a large scale, and after about 26 fractionations the hafnium contains not more than 1% of zirconium (de Boer, Z. anorg. Chem. 1926, 150, 210; with Broos, *ibid.* 1930, 187, 190).

A precipitation method has also been recommended by Prandtl (*ibid.* 1932, 208, 420; 1937, 230, 419) in which the solution of the hydroxides in dilute sulphuric acid containing ammonium sulphate and oxalic acid is treated with sodium ferrocyanide; hafnium is enriched in the head fractions. The presence of phosphate ions tends

to interfere by causing co-precipitation of phosphates.

Sublimation and distillation methods have also been employed. The double compounds  $2\text{XCl}_4 \cdot \text{PCl}_5$  and  $2\text{XCl}_4 \cdot \text{POCl}_3$  ( $\text{X} = \text{Hf}$  and  $\text{Zr}$ ), produced by molting together the mixed hafnium and zirconium tetrachlorides with the corresponding phosphorus chlorides, can be distilled under ordinary pressures and, in both cases, the hafnium compound, being the more volatile, is concentrated in the early fractions (Van Arkel and de Boer, *ibid.* 1924, 141, 289; B.P. 221802).

**Metallic Hafnium**, obtained by thermal decomposition of its iodide, has also been prepared from the double fluoride  $\text{K}_2\text{HfF}_6$  or the tetrachloride by reduction with metallic sodium; the oxide may be used if a mixture of calcium and sodium is employed as the reducing agent (Van Arkel and de Boer, *ibid.* 1925, 148, 345; de Boer and Fast, *ibid.* 1930, 187, 193).

**Physical Properties.**—Hafnium is a highly lustrous, ductile metal resembling zirconium in appearance and crystalline form (hexagonal system). The X-radiogram gives the side of the unit triangular prism as 3.32 Å. and its height as 5.46 Å., with axial ratio 1:1.64. It melts at 2220°C. while its density at room temperature is 13.3, the atomic volume being 13.42. Six isotopes have been indicated, weak lines at 174 and 176 with stronger lines at 177, 178, 179 and 180; the relative abundance of these is approximately 0.3, 5, 19, 28, 18 and 30%, respectively (Aston, Proc. Roy. Soc. 1935, A, 149, 396; Dempster, Physical Rev. 1939, [ii], 55, 794). The specific heat at low temperature has been measured by Cristescu and Simon (Z. physikal. Chem. 1934, B, 25, 273) who find that there is an anomaly with a sharp peak at 75° abs. The resistivity of hafnium is  $30 \cdot 10^{-6}$  ohm-cm. at 0°C.; no evidence of superconductivity was noticed at 1.35° abs. (de Boer and Fast, Z. anorg. Chem. 1930, 187, 193).

The spectrum of hafnium possesses a great number of lines, the persistent ones being 2513.0, 2516.9, 2641.4, 2773.4, 2820.2, 2898.3, 2916.5, 3072.9, 3134.8, 4093.2 Å.

**Chemical Properties.**—Although falling between zirconium and thorium in the periodic classification, hafnium more closely resembles, but is more basic than, the former. Its reactions with acids, halogens and other reagents are similar to those of zirconium and it shows a like tendency to form complex salts.

#### COMPOUNDS.

**Hafnium Dioxide (Hafnia),  $\text{HfO}_2$ .**—Obtained by ignition of the hydroxide, oxalate, oxychloride or sulphate. It is a diamagnetic oxide,  $d^{20}_D$  0.68, incandescent at high temperatures while its melting-point is  $3047 \pm 25^\circ$  abs. Hafnia is an amphoteric oxide and strontium hafnate,  $\text{SrHfO}_6$ , has been made (Hoffmann, Naturwiss. 1933, 21, 676).

**Hafnium Tetrafluoride,  $\text{HfF}_4$ .**—Monoclinic prismatic crystals obtained on heating ammonium hafnium fluoride,  $(\text{NH}_4)_2\text{HfF}_6$ , in a stream of nitrogen at 500°. It may be purified by sublimation at 800°, and this process leads to a partial separation from any zirconium present (Von Hevesy

and Dullenkopf, Z. anorg. Chem. 1934, **221**, 161; Schultze, Z. Krist. 1934, **89**, 477). When hafnia is dissolved in hydrofluoric acid and the solution is concentrated, crystals of the trihydrate  $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$  separate, and these when recrystallised several times from water hydrolyse to form the oxyfluoride  $\text{HfOF}_2 \cdot 2\text{HF} \cdot 2\text{H}_2\text{O}$  (Von Hevesy and Wagner, Z. anorg. Chem. 1930, **191**, 194). Hafnium fluoride very readily forms a series of double salts with alkali and ammonium fluorides of the types  $\text{M}_2[\text{HfF}_6]$  and  $\text{M}_3[\text{HfF}_7]$ ; these are more soluble in water than the corresponding zirconium salts.

**Hafnium Chlorides.**—Hafnium burns fairly readily when heated in chlorine, producing the tetrachloride  $\text{HfCl}_4$  as a white crystalline mass which can be further purified by sublimation in dry hydrogen. It begins to volatilise at  $250^\circ$  and any zirconium present will tend to collect in the first portion of the sublimate. The chloride is also formed when the oxide is heated in the presence of a reducing agent and chlorine. Water hydrolyses it to hafnyl chloride,  $\text{HfOCl}_2$ , while addition of ether to an alcoholic solution of the latter substance yields another oxychloride,  $\text{Hf}_2\text{O}_3\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ . These compounds are less soluble in hydrochloric acid than the zirconium analogues and have been used in the separation of the two metals (de Boer and Fast, l.c.).

**Hafnium Oxybromide** is formed as glistening tetragonal crystals on concentrating a solution of hafnia in hydrobromic acid. It is extremely soluble in the dilute acid, but increasing concentration of the latter causes a rapid decrease in the solubility. Thus in 0.35*N*-HBr at  $25^\circ$  the solubility is 3.3 g.-mol.  $\text{HfOBr}_2$  per litre while in 13.36*N* it is 0.0038 g.-mol. (Von Hevesy and Wagner, l.c.).

**Hafnium Iodide** (*see* de Boer, Z. anorg. Chem. 1926, **150**, 216).

**Hafnium Sulphate**, made either by the action of fuming sulphuric acid on the tetrachloride or by repeated evaporation of the fluoride with concentrated sulphuric acid, always seems to contain excess  $\text{H}_2\text{SO}_4$  over that required by the formula  $\text{Hf}(\text{SO}_4)_2$ . This excess can only be removed at a temperature ( $500^\circ$ ) at which the salt begins to decompose (Von Hevesy and Cremer, *ibid.* 1931, **195**, 339).

**Hafnium Nitrate.**—This salt, mixed with tungstic oxide, is employed in making lamp filaments. The hafnium produced is stated to prevent the recrystallisation of the tungsten filament.

**Hafnium Phosphates.**—When a solution of hafnyl chloride in 6*N*-HCl is added to one of disodium phosphate in the same medium a finely divided precipitate is produced corresponding to the formula  $\text{HfO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ . This might be either  $\text{Hf}(\text{HPO}_3)_2 \cdot \text{H}_2\text{O}$  or  $\text{HfO}(\text{H}_2\text{PO}_4)_2$ , but the well-known stability of hafnyl as compared with hafnium ions strongly favours the latter formula. When ignited, the salt loses 2 mol. of water yielding hafnyl metaphosphate,



Hafnyl phosphate is the least soluble of all phosphates in hydrochloric acid, the solubility in 6*N*-acid at room temperature being 0.00009 g.-mol.

per litre (Von Hevesy and Kimura, J. Amer. Chem. Soc. 1925, **47**, 2540; Z. angew. Chem. 1925, **38**, 228).

**Hafnium Carbide.**—Said to be obtained as a grey powder on heating an intimate mixture of hafnia and finely divided carbon in a graphite tube at  $2,000$ – $3,000^\circ\text{C}$ . or by passing the vapour of the tetrachloride together with methane and hydrogen over a heated tungsten filament.

**Hafnium Boride** has also been prepared (Agte and Moers, Z. anorg. Chem. 1931, **198**, 233; *see also* Vol. II, 44c).

**Hafnium Acetylacetonate**,  $\text{Hf}(\text{C}_5\text{H}_7\text{O}_2)_4$ .—Monoclinic crystals, m.p.  $194$ – $195^\circ$ ,  $d_4^{25}$  1.67, formed when acetylacetone and dilute soda solution are added to hafnyl chloride in water; the product is recrystallised from alcohol. It sublimes slowly in a high vacuum at  $82^\circ$  but at  $87^\circ$  decomposition sets in. Like zirconium acetylacetonate and unlike the thorium analogue it does not combine with ammonia; it further resembles the former in giving a decahydrate  $\text{Hf}(\text{C}_5\text{H}_7\text{O}_2)_4 \cdot 10\text{H}_2\text{O}$  (Von Hevesy and Logstrup, Ber. 1926, **59** [B], 1890).

**References.**—Georg von Hevesy, "Das Element Hafnium," Berlin, 1927; J. W. Mellor, "A Comprehensive Treatise on Inorganic and General Chemistry," Vol. VII, London, 1927; H. Rose, "Das Hafnium," Braunschweig, 1926. G. R. D.

**HAGLUND PROCESS** (Vol. 1, 268b).

**HAIDINGERITE** (Vol. II, 223b).

**HAIR DYES (HUMAN).** The practice of dyeing the hair has considerably increased of recent years, particularly since the introduction of organic intermediates such as *p*-phenylenediamine which can be oxidised to produce dyes on the hair. But the art is really of great antiquity; there are references to it in ancient Hebrew, Persian and Roman literature. The practice was common too in ancient Egypt and it seems that the use of mineral pigments such as kohl, and vegetable colours including henna, dates back several thousands of years.

Although hair has a general composition similar to that of wool, its dyeing presents peculiar problems because the affinity of human hair for dyes is very much less than that of wool, and the dyeing qualities of living hair differ somewhat from those of dead hair. Moreover, it will be obvious that only those substances can be used which will be effective at temperatures below about  $37^\circ\text{C}$ . and that the use of markedly acid or alkaline reagents will be fraught with serious consequences. There are three principal classes of hair dyes: (i) Inorganic dyes or pigments; (ii) Vegetable colouring matters; and (iii) Oxidation dyes.

(i) In this class the most ancient material is kohl, the name covering a variety of black pigments, including charcoal and various forms of galena. It is not now used, save perhaps in some theatrical make-ups, in which the pigment is made into a paste or emulsion with resinous materials, gum or gelatin. Lead compounds are still used rather extensively, though they are more often described as hair restorers. The chief ingredients in such mixtures are lead acetate, less commonly lead oxide, emulsified

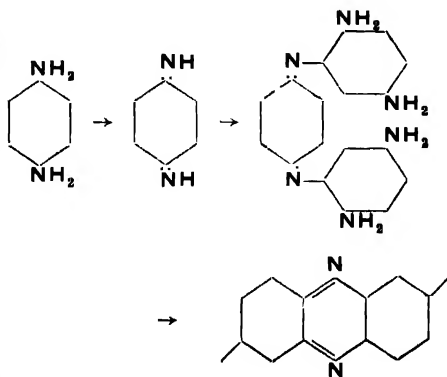


with a sulphur compound—either colloidal sulphur, sodium thiosulphate or a mixture thereof—in the presence of glycerin and oil. The proportions commonly present may be about 3% of lead acetate with an equal quantity of sulphur. These mixtures react slowly on the hair and form a brown or black coating of lead sulphide, part of which is adsorbed into the hair fibres. The mode of action is not quite clear, but it appears that the sulphur is first adsorbed and later combines with the lead. Silver forms the basis of another series of dyes; these differ from lead mixtures in that they require two separate solutions, one containing silver nitrate with or without ammonia, and the other containing either an alkaline sulphide or a solution of pyrogallol. Sulphide mixtures give light brown shades, while the pyrogallol mixtures are darker or even black. Bismuth has enjoyed quite a vogue. The basis is usually bismuth citrate dissolved in a water-alcohol-glycerin mixture, and a separate solution contains cholesterol, sulphur and albumin. As in the case of the lead pigments, the reactions involve changes in the keratin of the hair with the liberation of hydrogen sulphide and the formation of a black bismuth sulphide on the hair. Various claims have been made as to the function of the cholesterol and albumin, but there is no evidence that they participate in the reactions. Preparations based on nickel, cobalt, iron, manganese and copper salts also appear in the literature, but are not in common use, though they may, as noted below, be used in admixture with henna and other vegetable compounds. Salts of these metals may be employed in conjunction with pyrogallol, with which they are said to produce good black dyes.

(ii) The principal hair dyes coming within the second class, vegetable dyes, are henna, walnut, logwood, chamomile and indigo. Cutch and other tannin materials are used to a less extent. The dyeing properties of henna (*q.v.*) are due almost entirely to 2-hydroxynaphthaquinone, known also as *lawsone*; this substance is present to the extent of 1-1.5% and acts as an acid dye-stuff. It is a pale yellow in acid solution and dyes hair a bright orange colour, the shade being considerably affected by metallic mordants. For use the powdered leaves, about 5 oz. for a head, are made into a paste with boiling water and applied to the hair for about 15 minutes; the presence of a small amount of a wetting agent is of advantage. Many compounded Hennas are sold; these contain copper salts, pyrogallol or even *p*-phenylenediamine, and serve to give much darker shades than are obtainable from pure henna. Indigo finds use in conjunction with henna under the name of *henna-reng*. A mixture of 2 parts of indigo with 1 part henna gives a brown and 3 parts of indigo give a darker brown. For the composition of henna powder and methods for the determination of 2-hydroxynaphthaquinone, see H. E. Cox, Analyst, 1938, **63**, 397. Walnut shudes and leaves which also find use as a hair dye resemble henna in dyeing properties. The active ingredient is 5-hydroxynaphthaquinone, *juglone*; it dyes hair a dark brown but the colour takes some time to develop fully. Walnut is applied in the form of an extract, or the powdered leaves,

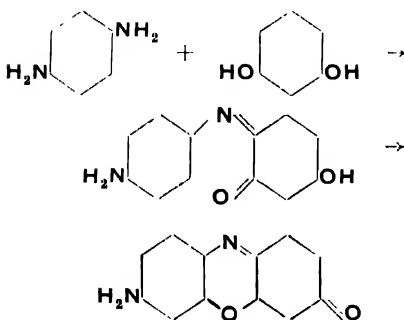
with or without henna, are mixed to make a paste which can be applied hot. Extract of walnut should be freshly prepared as it does not keep well; commercial products may contain metallic additions, notably silver salts. There have been several attempts to apply logwood as a hair dye, but it is not very successful unless in admixture. The preparations for production of a satisfactory colour on the hair from the hematoxylin present in logwood mixtures usually consist of powders containing the wood with additions of starch, chestnut or henna, and as oxidiser an acid solution of dichromate. Chamomile flowers (*q.v.*) contain a rather feeble dye-stuff of the flavone class called *apigenin*, the glucosidal constitution of which is described by Power and Browning (J.C.S. 1914, **105**, 1829). For practical application a hot paste made from powdered chamomile flowers diluted with fuller's earth or kaolin is applied to the hair and left in contact with it for half an hour or more. The colour produced on light hair is a warm blonde; it may be darkened by admixture with henna or walnut. Chamomile finds more extensive use as a shampoo or rinse than actually as a dye.

(iii) The most interesting development in hair dyeing began in 1888 when Erdmann introduced the use of *p*-phenylenediamine, the first and most important member of the oxidation class. Since that date a very great number of substances have been proposed or patented which claim to possess special merit, or to avoid the one disadvantage of *p*-phenylenediamine, namely its occasional irritant effect on the skin. Dye mixtures of this class involve two reagents, one being an alkaline solution of the base or bases, usually mixed with soap or other wetting agent and perfume, and the other a solution of hydrogen peroxide or tablets of urea peroxide. These two solutions are mixed immediately before use and are applied with a brush to the well-washed hair. When *p*-phenylenediamine is thus oxidised in alkaline solution the first product is Bandrowski's base (Ber. 1894, **27**, 480) possibly with quinonediimine as an intermediate product; this subsequently condenses with the formation of a complex azine in and on the hair fibres (*cf.*



H. E. Cox, Analyst, 1934, **59**, 3). When *p*-phenylenediamine is used alone the range of colours obtainable is limited to dull brown, greys

and black, and there is considerable wastage. To extend the range and obtain auburn, light and dark brown shades, a dihydric phenol is added. This is usually resorcinol or catechol, but a variety of other compounds may be used. In the presence of such phenols the course of the reaction is quite different; there is no formation of Bandrowski's base but of indophenols of a red-brown colour, and having the oxygen in the *ortho*-position to the nitrogen. These indophenols further condense to oxazones on the hair (*cf.* Cox, *ibid.* 1940, **65**, 393), and produce a pleasing variety of shades. The popularity of



these mixtures is such that it has been stated that 10 million packets per annum are sold in one European country, and as might be expected, there are many variants of the mixtures which give rise to particular colours or for which special virtues are claimed. The success of *p*-phenylenediamine as a hair dye is somewhat offset by the fact that it produces a troublesome dermatitis on some few individuals who are idiosyncratic or supersensitive (*cf.* Ingram, *J. Derm. Syph.* 1932, **44**, 422; Cox, *J. Med. Legal Soc.* 1937, 123). For this reason the substance and its homologue *p*-toluylenediamine are included in Part II of the Poisons Rules in Britain and are subject to legislative restrictions in France, Germany and the U.S.A. It is customary, when these dyes are to be used, first to make a small patch test on the individual and only to proceed if this test indicates that no supersensitivity exists. Perhaps it is partly as a result of this difficulty that intensive search has been made for other oxidisable intermediates which might have the same or better tinctorial power and, in addition, possess all the virtues required of the ideal hair dye, viz. (1) it should provide a good range of colours and a silky lustre on the hair; (2) it must not make the hair brittle; (3) it must not irritate or stain the scalp; (4) it must not fade or produce "off" colours; and (5) it must not interfere with subsequent permanent waving of the hair. Of the members of the same series *p*-toluylenediamine is used and *p*-xylylenediamine has been suggested. Then sulphonic acid groups have been introduced to reduce toxicity but such compounds are of inferior tinctorial power, so also are the acetyl derivatives. The methyl-, ethyl- and dimethyl-derivatives of *p*-phenylenediamine are very good dye bases but, so far as is known, they are not less toxic than the original base. The

aminophenols, aminoanisoles and aminophenotols are also used; *p*-aminophenol will produce a good brown. 2:4-Diaminophenol is also useful. Another interesting series includes the nitroamines such as 2-nitro-4-amino- and 2-amino-4-nitro-phenol and nitro-*p*-phenylenediamine; the chemistry of the oxidation of these compounds has not yet been elucidated. Various diphenyl-derivatives also find use; such are the *p*-aminodiphenylamines, *pp'*-diaminodiphenylamine and their substitution products and the naphthalenediamines. These are also blended with a dihydric or trihydric phenol to give the required range of colours. Any of these compounds may be present in mixtures together with a number of other substances whose names appear in the now voluminous list of patents. Ready-formed synthetic dyes may also be present.

In view of what has been said it is clear that no simple methods of analysis can be prescribed which will cover all cases. Mixtures will contain in addition to the foregoing bases suitable quantities of wetting agents, ammonia, soaps or sulphonated compounds, perfumes and sometimes glycerin or oils. Before applying specific tests therefore it is necessary to separate the ingredients, as diamines form addition compounds with dihydric phenols and various interactions are possible in the solutions, thus rendering colour reactions most unreliable. Much can be effected by judicious selection of solvents; petroleum spirit extracts any fat or fatty acids from the acidified mixture and subsequent treatment with ether will remove most of the dihydric phenol, after which addition of alkali in the presence of a mild reducing agent will enable any diamine to be extracted. These various fractions can be further separated and examined. In checking by means of nitrogen determinations it should be borne in mind that some of these derivatives give markedly low results with the Kjeldahl process. J. Carol (*J. Assoc. Off. Agr. Chem.* 1940, **23**, 821) gives a good method for the separation of *p*-phenylenediamine in such mixtures.

In general finished dyes such as are useful for textiles have very limited affinity for living hair under the conditions which must be observed in hair dyeing. There are, however, considerable numbers of tinting mixtures or rinses which find extensive use for fancy purposes. It is important that dyes used for this purpose should be of a good degree of purity.

**References.**—Redgrove and Bari - Woollss "Hair Dyes and Hair Dyeing," W. Heinemann, Ltd., London, 1939, and various papers by Cox (*l.c.*) H. E. C.

"HALARSOL" (Vol. I, 489b).

"HALAZONE" (Vol. IV, 20c).

**HALBERG-BETH** system of dry gas-cleaning (Vol. V, 377).

**HALF VALUE PERIOD.** This term (or the equivalents "half life period" and "half time") is used with reference to processes which take place at a measurable speed, and represents the time necessary for some quantity which is being measured to decrease to one-half of its original value. The commonest case is that of a chemical reaction, where the half value period

(H.V.P.) is the time necessary for the concentration of one of the initial reactants to be reduced to one-half. If, as is often the case, the course of the reaction is being followed by measuring the value of some property (e.g. pressure, volume, colour, conductivity, etc.) which is proportional to the concentration of the reactant, then the H.V.P. is also equal to the time necessary for this value to become halved. This criterion is often applied to radioactive changes, where the activity of the specimen is the property measured; similarly, in a racemisation the H.V.P. is the time required for the initial optical rotation to become halved.

The dependence of the H.V.P. on the initial concentration, and its relation to the velocity constant, depend on the kinetic order of the change. If  $a$  is the initial concentration of the reactant and  $x$  its concentration after time  $t$ , then for *first order reactions* (which include simple radioactive changes)

$$\frac{dx}{dt} = -k_1x, \quad k_1t = \log_e \frac{a}{x}, \quad t_1 = \frac{1}{k_1} \log_e 2,$$

so that the H.V.P. is independent of the initial concentration and inversely proportional to the first order constant  $k_1$ . In this case the reaction velocity can be defined equally well by either  $k_1$  or  $t_1$ , and in the case of radioactive changes the latter is more often used. For a *second order reaction*,

$$\frac{dx}{dt} = -k_2x^2, \quad k_2t = \frac{1}{x} - \frac{1}{a}, \quad t_2 = \frac{1}{ak_2}.$$

The H.V.P. is now inversely proportional both to the initial concentration and to  $k_2$ . In general, for a reaction of the  $n$ th order ( $n > 1$ ),

$$\frac{dx}{dt} = -k_nx^n, \quad k_nt = \frac{1}{n-1} \left( \frac{1}{x^{n-1}} - \frac{1}{a^{n-1}} \right),$$

$$t_1 = \frac{2n-1}{(n-1)a^{n-1}k_n}.$$

Thus, for all reaction orders, the H.V.P. of a reaction of the  $n$ th order is inversely proportional to  $a^{n-1}$ , where  $a$  is the initial concentration (or, in the case of a gas, the initial pressure). The dependence of the H.V.P. upon the initial concentration or pressure can thus be used as a method of determining the kinetic order of a change, though it is usually desirable to supplement this by measurements on the course of single reactions.

pits or etched figures are readily produced on the cube faces by solution. Silky, fibrous masses also occur. But most frequently the mineral is found as granular or sparry masses with bright cleavage surfaces. This perfect cleavage, parallel to the faces of the cube, is an important character. In addition, the crystals sometimes break along surfaces (glide-planes) parallel to the rhombic-dodecahedron. This effect is, however, secondary, and is only produced after the crystal has been subjected to pressure, either naturally by earth movements or by artificial means. If a cleavage cube of salt be placed diagonally in a vice so that two cube edges are held by the jaws, it can be broken in this direction. The plastic deformation of rock-salt and the percussion-figure (a four-rayed star with the rays parallel to the diagonals of the cube face, which is produced on a cleavage surface by a smart blow with a blunt point) also depend on the presence of these planes of gliding.

Crystals are usually colourless and transparent, but occasionally they are of a deep blue or violet colour. This colour disappears when the salt is dissolved in water or when heated; and it can be produced artificially by the vapour of alkali metals or by the action of cathode or radium rays. It has been variously ascribed to the presence of metallic sodium, sodium subchloride,  $\text{Na}_2\text{Cl}$ , or sulphur. Sp.gr. of pure crystals, 2.17; hardness  $2\frac{1}{2}$ ; specific heat, 0.219. The mineral is a non-conductor of electricity and is highly diathermanous. It is therefore used as blocks and lenses for experiments on radiant heat. The best crystallised material is obtained from Stassfurt in Prussia, and from Wieliczka and Kalusz in Poland; good, clear cleavage blocks have been found at Meadowbank in Cheshire. Crystals are very nearly pure sodium chloride, and mixed crystals with potassium chloride (sylvite) do not occur. Massive material contains impurities of various kinds. A variety known as *huantajayite*, containing  $\text{AgCl}$  11%, is found as small cubes at Huantajaya near Tarapaca in Chile.

Rock-salt is most frequently found as bedded deposits in sedimentary rocks, such as sandstone, shale, clay and, less often, limestone, and is frequently associated with beds of gypsum and anhydrite, and sometimes with petroleum. Such deposits have evidently been formed in inland seas and lakes under desert conditions; they are of world-wide distribution and are met with in formations of all geological periods, as indicated below:

R. P. B.  
**HALITE or ROCK-SALT** (Fr. *Sel gemme*; Ger. *Steinsalz*). Sodium chloride,  $\text{NaCl}$ , crystallised in the cubic system. Although known as a mineral since remote times and of very wide distribution, the name halite (from  $\alpha\lambda\varsigma$ , salt) is comparatively recent (E. F. Glocker, 1847). Well-developed crystals with the form of simple cubes are not uncommon, but those of octahedral habit are quite rare. The faces of the cube sometimes show sunken depressions, though not so marked as in the hopper-shaped crystals produced artificially. Small square

Geological formations.	Localities.
Recent . .	Dead Sea, Caspian Sea, Great Salt Lake of Utah, California, etc.
Pliocene . .	Volterra in Tuscany, Parajd in Transylvania.
Miocene . .	Wieliczka and Kalusz in Poland, Bukovina, Minglanilla in Spain.

Geological formations.	Localities.
Oligocene . .	Eastern Carpathians in Transylvania, Wittelsheim in Alsace.
Eocene . .	Cardona near Barcelona, Caucasus, Rumania.
Cretaceous . .	Unna in Westphalia, Medea in Algeria, Texas, Louisiana, Peru.
Jurassic . .	Bex in Switzerland, Rodenburg in Hesse-Nassau, Peru.
Triassic— Keuper .	Cheshire, Worcestershire, Lancashire, north-east Yorkshire, Durham, Isle of Man, Antrim, Pyrenees, Lorraine, Celle in Hanover, Berchtesgaden in Bavaria, Hall in Tyrol, Hallein in Salzburg, Ischl and Hallstatt in Upper Austria, Aussee in Styria.
Muschelkalk	Friedrichshall in Württemberg, Ernstshall in Thuringia.
Bunter . .	Schöningen in Brunswick, Arnshall in Thuringia.
Permian . .	Stassfurt, Halle, etc., in Prussian Saxony, Artern in Thuringia, Sperenberg near Berlin, Segeberg in Holstein, Inowrazlaw in Posen, Orenburg in Russia, Kansas.
Carboniferous	Pennsylvania, Virginia, West Virginia, Michigan, Ohio, New Brunswick, Nova Scotia.
Devonian . .	Westphalia, Baltic provinces of Russia, Siberia, China.
Silurian . .	New York, Michigan, Ohio, Ontario.
Cambrian . .	Salt Range in Punjab.

In addition to these bedded deposits of rock-salt, which are the only deposits of economic importance, mention may be made here of some other modes of occurrence. The microscopic cavities present in vast numbers in the quartz of granitic igneous rocks often contain minute cubes of halite together with water and liquid carbon dioxide. The saline encrustations of active volcanoes (e.g. Vesuvius), produced either by direct sublimation or by the action of acid vapours on the scoria, contain sodium and potassium chlorides, usually in a powdery form, but occasionally as distinct crystals of halite and sylvite.

*References.*—For a detailed *résumé* of the mineralogical characters and occurrence of halite, see C. Hintze, "Handbuch der Mineralogie," Leipzig, 1911, Vol. I, pp. 101-231; on the deposits worked commercially, see J. O. von Buschman, "Das Salz, dessen Vorkommen und Verwertung in sämtlichen Staaten der Erde," 2 vols, Leipzig, 1906-9; A. F. Calvert, "Salt in Cheshire," London, 1915.

**HALLOYSITE.** A clay-mineral with approximately the composition of kaolinite (*q.v.*)

but containing rather more water (about 19%). It forms compact masses with a slight greasy feel and lustre, and may be white, grey or shades of various colours; sp.gr. 2.0-2.2; hardness 1-2. It occurs as beds in sedimentary rocks and as masses in mineral-veins, and has sometimes been observed as a decomposition product of granite and other rocks containing felspar. Possibly the minute amorphous granules of china-clay and some other clays may be referable to this species. (See H. Ries, "Clays, their Occurrence, Properties and Uses," 3rd ed., 1927; also Vol. III, 196a).

L. J. S.  
**HALOGEN ACETIC ACIDS.** Derivatives of acetic acid in which the hydrogen of the methyl group is partly or wholly replaced by a halogen.

#### CHLOROACETIC ACIDS.

**Monochloroacetic Acid,  $\text{CH}_2\text{Cl}\cdot\text{COOH}$ .**—The acid may be prepared by passing chlorine into 100 g. glacial acetic acid, 1 g. iodine, 2 g. red phosphorus and 2 g. phosphorus pentachloride at 100° contained in a flask fitted with a leading tube, a condenser and mechanical stirrer (Brückner, Amer. Chem. Abstr. 1930, 24, 61; Lyubarskii, *ibid.* p. 827; Shilov, *ibid.* p. 827). Sulphur, phosphorus, sulphur monochloride and acetic anhydride may also be used as catalysts (U.S.P. 1757100). Many patents protect the preparation from trichloroethylene by heating with sulphuric acid (U.S.P. 1304108, 1322898; B.P. 132042; see also J.S.C.I. 1922, 41, 191a).  $\alpha$ -Trioxymethylene and sulphuryl chloride at 170° in the presence of zinc chloride also give the  $\alpha$ -acid (Fuchs and Katscher, Ber. 1924, 57 [B], 1256).

The acid crystallises in three modifications:  $\alpha$ -, prisms, m.p. 61.3°;  $\beta$ -, plates, m.p. 56.18°;  $\gamma$ -, m.p. 50.20° (Muller, J. Physical Chem. 1914, 86, 197); b.p. 189°/77 mm., 104-105°/20 mm.;  $d_4^{20}$  1.3518 (Grinakowski, Chem. Zentr. 1913, II, 2076). For hydrates, see Colles (J.C.S. 1906, 89, 1252); heat of solution, Pickering (*ibid.* 1895, 67, 665) and Louguine (Ann. Chim. Phys. 1879, [v], 17, 251); heat of combustion 171.0 kg.-cal., Berthelot (Ann. Chim. Phys. 1893, [vi], 28, 567); electrical conductivity, Kortright (Amer. Chem. J. 1896, 18, 308); magnetic rotation, Perkin (J.C.S. 1896, 69, 1236); for the esterification velocity constant, see Sudborough and Lloyd (*ibid.* 1899, 75, 476); for electrolytic dissociation constant,  $K=1.55 \times 10^{-3}$ , see Ostwald (Z. physikal. Chem. 1889, 3, 176).

The acid is soluble in cold water, but decomposes on heating the solution into hydrochloric and glycollic acids (Buchanan, Ber. 1871, 4, 340, 863; Fittig and Thomson, Annalen, 1880, 200, 75; Senter, J.C.S. 1907, 91, 460). Metallic hydroxides of the type  $\text{R}^{\text{OH}}$  decompose it, yielding glycollic acid, whilst those of the type  $\text{R}^{\text{OH}}$  yield diglycollic acid (Schreiber, J. pr. Chem. 1876, [ii], 13, 346). The anhydride is produced by distilling the acid *in vacuo* with phosphorus pentoxide (Bischoff and Walden, Ber. 1894, 27, 2949). With ammonia glycine is produced (Kraut, Goldberg and Kunz, Annalen,

1891, 266, 295), and phenols in the presence of alkali give aryloxy-acetic acids (Giacosa, J. pr. Chem. 1879, [ii], 19, 396).

By reaction with sodium sulphide and sulphur in alkaline solution, dithioglycollic acid is produced which on reduction yields thioglycollic acid (G.P. 180875; J.C.S. 1907, 92, i, 1008). The sodium salt or the ethyl ester reacts with potassium cyanide to yield the corresponding derivatives of cyanacetic acid (Phelps and Tillotson, Amer. J. Sci. 1908, [iv], 26, 267, 275). The acid chloride, b.p. ca. 105°,  $d_4^{15}$  1.495 (Wurtz, Ann. Chim. 1857, [iii], 49, 61) may be prepared from the acid and thionyl chloride (de Barry Barnett, Chem. News, 1921, 122, 220). The use of methyl (b.p. 133°), ethyl (b.p. 143–145°), isopropyl (b.p. 147–155°) and *sec*-butyl (b.p. 165–170°) esters as fumigants has been investigated (Roark and Cotton, Ind. Eng. Chem. 1928, 20, 513; Nelson, *ibid.* 1380). The esters are obtained by passing the vapour of the alcohol, or a mixture of the alcohol and acid, through the molten acid, Ti, Th or Al salts promoting the reaction (Jap. P. 43731).

**Dichloroacetic Acid,  $\text{CHCl}_2\text{COOH}$ .**—This acid may be prepared in 80–85% yield by the action of copper powder on trichloroacetic acid in water or benzene (Doughty, J. Amer. Chem. Soc. 1925, 47, 1091; 1931, 53, 1594); or by the interaction of sodium cyanide (2 mol.) and chloral hydrate (1 mol.) in boiling aqueous solution, acidifying and extracting (A. 1929, 63). Also from asymmetric dichloroacetone with nitric acid (U.S.P. 2051470; Chem. Zentr. 1936, II, 3468).

Colourless liquid, b.p. 194°; 144°/164 mm.; 125°/70 mm.; 102°/20 mm.; 94°/1.1 mm.  $K = 5.14 \times 10^{-2}$ .

**Methyl Ester.**—B.p. 143–144°; 49.8–50°/2 mm.

**Ethyl Ester.**—B.p. 158°. Prepared by treating chloral in alcoholic solution with potassium cyanide (Chattaway and Irving, J.C.S. 1920, 1038) or from alcohol and dichlorovinyl ethers (G.P. 209268, 210502, 212592; J.C.S. 1909, 96, i, 453, 694, 873).

**Trichloroacetic Acid,  $\text{CCl}_3\text{COOH}$ .**—Prepared by chlorination of acetic acid at 120° in the presence of sulphur, phosphorus or iodine as catalyst; or by the oxidation of chloral with fuming nitric acid (Kolbe, Annalen, 1846, 54, 183) or chromic acid (Clermont, Compt. rend. 1873, 76, 774) or potassium permanganate (*idem.*, *ibid.* 1878, 86, 1270).

Deliquescent crystals, m.p. 58°, b.p. 196.5° 141–142°/25 mm.  $K = 1.2$ ; sp.g. 1.6298 at 60.6°. Heat of combustion (constant pressure) 92.8 kg.-cal. (Berthelot, Ann. Chim. Phys. 1893, [vi], 28, 569). Electrical conductivity (Rivals, Compt. rend. 1897, 125, 274; Ostwald, Z. physikal. Chem. 1887, 1, 100; 1889, 3, 177). The acid is readily hydrolysed to chloroform and carbon dioxide by heating with water or alkalis (Dumas, Annalen, 1839, 32, 101).

The acid has been used with success as a protein precipitant (Cristolet *al.*, Bull. Soc. Chim. biol. 1922, 4, 267) and also in toxicology for the isolation of alkaloids which might be destroyed by sulphuric acid (Florence, Bull. Soc. chim. 1927, [iv], 41, 1097). Its distribution co

efficients between water and various organic solvents have been determined (Anderson, A. 1929, 998) and also its solubility in different solvents (Kendall, Davidson and Adler, J. Amer. Chem. Soc. 1921, 43, 1487). Treatment with zinc in aqueous solution gives a quantitative yield of zinc dichloroacetate (Doughty, *ibid.* 1929, 51, 852). The sodium or zinc salt yields on electrolysis trichloromethyl trichloroacetate (Elbs and Kratz, J. pr. Chem. 1897, [ii], 55, 502). It forms compounds with aldehydes and ketones (Koboseff, J. Russ. Phys. Chem. Soc. 1903, 35, 652; Plotnikoff, *ibid.* 1904, 36, 1088; 1905, 37, 875; Ber. 1906, 39, 1794). For molecular compounds of trichloroacetic acid with alcohols, phenols and ethers, see Pushin and Rikowski, Annalen, 1935, 516, 286.

The acid has been shown to undergo the Reimer-Tiemann reaction with phenols, but the yields are poor (Van Alphen, Rec. trav. Chim. 1927, 46, 144).

**Methyl Ester.**—B.p. 152.3–152.5°/763.3 mm. (Schiff, Z. physikal. Chem. 1887, 1, 379; Anschütz and Haslam, Annalen, 1889, 253, 124);  $d_4^{15}$  1.4892 (Henry, J.C.S. 1885, 48, 1121).

**Ethyl Ester.**—B.p. 164°;  $d_4^{15}$  1.369 (Claus, Annalen, 1878, 191, 58; Brihl, *ibid.* 1880, 203, 22; Schiff, *ibid.* 1883, 220, 108).

The cobalt, manganese and cadmium salts of the chloroacetic acids have been prepared by neutralising the acid with the metal carbonate and evaporating in a vacuum desiccator (Amer. Chem. Abstr. 1929, 23, 3900), and also the uranyl salts (A. 1926, 372).

## BROMOACETIC ACIDS.

### Monobromoacetic Acid, $\text{CH}_2\text{BrCOOH}$ .

Prepared in 80% yield from 20 g. acetic acid, 58 g. bromine and 0.4 g. red phosphorus as catalyst, at 100–105° (Amer. Chem. Abstr. 1922, 16, 2842); m.p. 50°; b.p. 203°; 168°/250 mm.; 118°/15 mm.;  $K = 1.38 \times 10^{-3}$  at 25°C. For electrical conductivity, see Ostwald, Z. physikal. Chem. 1889, 3, 178; Kortright, Amer. Chem. J. 1896, 18, 368.

The aqueous solution decomposes slowly on heating, giving glycollic acid (Senter, J.C.S. 1909, 95, 1828). The sodium salt heated *in vacuo* yields glycollide. Much work has been done on the physiological action of the acid and its esters.

**Methyl Ester.**—Prepared by heating the acid and alcohol in sealed tubes at 100° (Perkin and Duppa, Annalen, 1858, 108, 109); b.p. 144° with decomposition.

**Ethyl Ester.**—Prepared as the methyl ester or from ethyl alcohol and bromoacetylchloride (Gal, Annalen, 1864, 132, 179); b.p. 159°.

*p*-Nitrobenzyl Ester has m.p. 88–89°.

### Dibromoacetic Acid, $\text{CHBr}_2\text{COOH}$ .

May be prepared by dropping bromine into boiling acetic acid to which 5% of sulphur has been added, and finally raising the temperature to 150° (Genveasse, Bull. Soc. chim. 1892, [iii], 7, 365); m.p. 48°; b.p. 232–234° (with decomposition); 195–197°/250 mm. Easily soluble in water and alcohol.

**Ethyl Ester.**—Prepared from anhydrous sodium acetate (1 mol.), bromalecanhydride (1 mol.)

and absolute alcohol (Klebs, Z. physikal. Chem. 1896, 19, 303); b.p. 192–194°; 120–121°/74 mm.

**Tribromoacetic Acid,  $\text{CBr}_3\cdot\text{COOH}$ .**—Prepared by gently warming bromal with fuming nitric acid and allowing the mixture to stand for 1 hour (Schaffer, Ber. 1871, 4, 370).

Monoclinic prisms, m.p. 130°, b.p. 245° (with decomposition). The acid is decomposed by water to give bromoform and carbon dioxide exclusively (De Groote, Bull. Soc. chim. Belg. 1928, 87, 225).

**Ethyl Ester.**—Prepared by passing hydrogen chloride into a cooled alcoholic solution of tribromoacetic acid (Broche, J. pr. Chem. 1894, [ii], 50, 98); b.p. 225°; 148°/73 mm.

#### CHLOROBROMOACETIC ACIDS.

##### Chlorobromoacetic Acid, $\text{CHClBr}\cdot\text{COOH}$ .

Prepared by heating equimolecular quantities of monochloroacetic acid and bromine in sealed tubes at 160° (Cech and Steiner, Ber. 1875, 8, 1174). Also prepared by the hydrolysis of the acid chloride obtained by the action of bromine on  $\alpha\beta$ -dichlorovinyl ether (Backer and Mook, J.C.S. 1928, 2125). Also by heating chlorobromomalonic acid at 130° until evolution of  $\text{CO}_2$  ceases (Read and McMath, *ibid.* 1926, 2183); m.p. 31.5°, b.p. 214.5° (decomp.), 103–104°/11 mm. (Backer and Mook, *l.c.*); m.p. 38° (Read and McMath, *l.c.*); b.p. 210–212° (Vanderstichele, *ibid.* 1923, 123, 1227). It is extremely deliquescent. Backer and Mook (*l.c.*) completed the resolution of this acid, employing quinine for isolating the dextro and brucine for isolating the levo isomer, respectively.

**Amide**, m.p. 126°. **Ethyl ester**, b.p. 174°. **Phenyl ester**, m.p. 46.5°, b.p. 266° (Crompton and Triffitt, *ibid.* 1921, 119, 1874).

##### Monochlorodibromoacetic Acid, $\text{CClBr}_2\cdot\text{COOH}$ .

Prepared by heating monochlorodibromoacetaldehyde with fuming nitric acid (Neumeister, Ber. 1882, 15, 603); m.p. 89°; b.p. 232–234° (with decomposition). Potassium hydroxide converts it, on heating, into monochlorodibromomethane.

##### Dichloromonobromoacetic Acid, $\text{CCl}_2\text{Br}\cdot\text{COOH}$ .

Prepared from dichloromonobromoacetaldehyde and fuming nitric acid (Neumeister, *ibid.* 1882, 15, 603); m.p. 64°; b.p. 215° (decomposition).

#### iodoacetic Acids.

**Moniodoacetic Acid,  $\text{CHI}\cdot\text{COOH}$ .**—Prepared from monochloro- or monobromoacetic acid and sodium iodide in acetone (G.P. 230172, Chem. Zentr. 1911, 1, 359), or from potassium iodide and chloroacetic acid in water at 50° (Kailan and Jungermann, *ibid.* 1934, II, 3240). Also by hydrolysis of the ethyl ester (*q.v.*) with baryta water (Perkin and Duppa, Annalen, 1859, 112, 125); m.p. 82°.

**Ethyl Ester.**—Prepared by the interaction of ethyl chloro- or bromoacetate, potassium iodide and alcohol (Perkin and Duppa, *l.c.*); b.p.

69°/12 mm.; 75–78°/16 mm. The acid and its ester possess marked poisonous properties (Chlopin, Amer. Chem. Abstr. 1928, 22, 127, 649).

**Methyl Ester.**—Prepared in a manner analogous to the ethyl ester; b.p. 169–171°. **sec-Octyl Ester**, b.p. 146°–147°/17 mm. (Rule and Mitchell, J.C.S. 1925, 3202).

The neutral ammonium salt (McMaster and Pratte, J. Amer. Chem. Soc. 1923, 45, 2999) and a basic ferric salt (A. 1926, 949) have been prepared.

**Di-iodoacetic Acid,  $\text{CHI}_2\cdot\text{COOH}$ .**—Prepared by the interaction of 1 part of malonic acid with 1 part of iodic acid in 4 parts of water; carbon dioxide is evolved; the solution is cooled, filtered and allowed to stand. After 2 or 3 days crystals of tri-iodoacetic acid separate; these are filtered off and, after heating the filtrate, the di-iodo compound separates on cooling; m.p. 110° (Angeli, Ber. 1893, 26, 596).

**Ethyl Ester.**—Prepared by the interaction of ethyl dibromoacetate and potassium iodide in alcoholic solution (Perkin and Duppa, Annalen, 1861, 117, 351), or of ethyl dichloroacetate and calcium iodide (Spindler, *ibid.* 1885, 231, 273). Yellow liquid, which cannot be distilled unchanged under atmospheric pressure.

**Tri-iodoacetic Acid,  $\text{CI}_3\cdot\text{COOH}$ .**—For preparation, see di-iodoacetic acid. Yellow plates, m.p. 150° with decomposition. By heating with acetic acid, iodoform and carbon dioxide are produced.

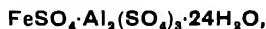
#### FLUOROACETIC ACIDS.

**Trifluoroacetic Acid,  $\text{CF}_3\cdot\text{COOH}$ .**—Prepared by the oxidation of trifluorotoluidine (Swarts, Bull. Acad. roy. Belg. 1922, [v], 8, 343; Chem. Zentr. 1923, III, 918).

For the preparation of the *ethyl ester* (b.p. 126°) of trifluoroacetic acid, see Ray and Ray, *ibid.* 1937, I, 3627. Electrolysis of trifluoroacetic acid gives hexafluoroethane (Swarts, Bull. Acad. roy. Belg. 1931, [v], 17, 27). Treatment of the silver salt in ice-cold 30% solution in benzene with iodine gave the anhydride (Swarts, Amer. Chem. Abstr. 1930, 24, 589).

**Ethyl Fluorodibromoacetate.**—Prepared by the reaction of 1 mol. ethyl tribromoacetate and 4 mol. silver fluoride at 190–200°. It is an insoluble liquid and readily hydrolysed by water (Rathbury, Ber. 1918, 51, 669).

#### HALOTRICHITE,



occurs naturally as silky, fibrous, efflorescent masses of a yellowish-white colour; named from  $\alpha\lambda\varsigma$ , salt, and  $\theta\rho\iota\varsigma$ ,  $\tau\rho\iota\chi\acute{o}\varsigma$ , hair. It results by the action of the products of decomposition of pyrite on surrounding aluminous rocks, as at Hurler and Campsie near Glasgow; and also by the action of volcanic gases on rocks, as at the Solfatara di Pozzuoli near Naples, and in Iceland, where a variety called “hver-salt” is found. A large deposit occupies the crater of an extinct volcano near the source of the Gila river in Grant Co., New Mexico. At Urmia in Persia the mineral has been used for making ink.

L. J. S.

**HALOXILINE** (Vol. IV, 463b).

**HALPHEN-HICKS REACTION** (Vol. III, 295a).

**HALPHEN TEST** (Vol. II, 167b).

**HALVORSAN PROCESS** (Vol. I, 268c).

**HAMAMELIN.** (*Extract of Hamamelis B.P.C.*) A solid extracted by alcohol from the dried leaves of *Hamamelis virginiana* Linn. and used in medicine as an astringent, principally in the treatment of piles. The drug occurs in the form of a green or almost black powder; the brown substance formerly appearing in commerce under this name was prepared from hamamelis bark. Berry (Pharm. J. 1936, 2, 247) suggested improvements in manufacture to ensure maximum solubility and activity.

A. D. P.

**HAMAMELIS.** The dried leaves of the witch-hazel, *Hamamelis virginiana* Linn., a shrub indigenous to North America. The drug contains *tannin*, *gallic acid* and a trace of a *volatile oil*. Liquid and solid extracts prepared from the drug are used in medicine as astringents (*v.* HAMAMELIN). The fresh leaves of the witch-hazel are used to prepare a distilled extract (*Liquor Hamamelidis B.P.C.*), a weakly alcoholic, colourless liquid, possessing the characteristic odour of witch-hazel, but practically devoid of tannin. It is used externally in medicinal and cosmetic applications for the treatment of sunburn and other skin troubles. *Hamamelis bark (Hamamelidis Cortex B.P.C.)* is no longer an official pharmacopoeial drug, but is still used in medicine in the form of a tincture (*Tinctura Hamamelidis B.P.C.*). The bark contains about 6% of *tannins*, including crystalline *hamamelitannin*, *gallic acid*, *resin*, *fat* and *phytosterol*. For description of hamamelitannin and its derivatives, see Freudenberg and Blümmel (Annalen, 1924, 440, 45); Schmidt (*ibid.* 1929, 476, 250).

A. D. P.

**HAMMELOSE** (Vol. II, 288d).

**HAMBERGITE** (Vol. I, 685a).

**HAMLINITE** (Vol. V, 263c).

**HANSA YELLOWS** (Vol. IV, 235a).

**HARDEN AND YOUNG ESTER** (Vol. V, 20d, 22d).

**HARDENED OR HYDROGENATED FATTY OILS.** The scarcity of natural solid fats compared with the relative abundance of liquid oils is one of the outstanding features of the fatty oil trades. This unequal distribution has caused a greater value to be attached to the solid fats, and, with increasing demand for edible oils, there has arisen a desire for methods of producing solid fats from liquid material. Chemically the main difference between these two classes of fatty product is a preponderance of saturated long chain fatty acid esters (glycerides) in the solid fats and of corresponding unsaturated compounds in the oils.

The successful reduction of the unsaturated esters by catalytic hydrogenation is probably the most important development in the oil industry of the last 30 years. Prior to the introduction of this process various methods had been tried, Varrontrapp's reaction forming the basis of one of the most interesting. According to this oleic acid is converted to palmitic acid by

fusion with alkali hydroxide. In practice the process was limited to the treatment of fatty acids and was not applied to neutral glycerides. It yielded material of poor colour and the large volumes of hydrogen liberated were a source of danger.

Schmidt's process of heating oleic acid with zinc chloride at 185° requires a distillation of the product, and this is attended by partial decomposition of the  $\beta$ -hydroxystearic acid formed in the reaction, into oleic and *iso*oleic acids. Better results were obtained by methods in which oleic acid was treated with sulphuric acid at a low temperature, and the resulting sulphonated compound decomposed by means of water into hydroxystearic acid and free sulphuric acid. By distillation of the hydroxystearic acid a mixture of oleic acid and its solid isomeride *iso*oleic acid was obtained, the latter being of commercial value as a candle material.

In 1897 Tissier (F.P. 263158, 1897) claimed a process of converting oleic acid into stearic acid by means of the nascent hydrogen liberated when fats are heated, in an autoclave, with water and finely divided zinc; but Freundlich and Rosauer (Chem.-Ztg. 1900, 24, 506) found that the process did not produce the results claimed for it.

Electrolytic methods of hydrogenating oleic acid are claimed in the patents of Magnier, Brangier and Tissier (B.P. 3363, 1900) and of Hemptinne (B.P. 1572, 1905). According to the latter, oleic acid is spread in a thin layer on metallic plates, between which is passed a silent discharge, whilst the air in the vessel is replaced by hydrogen. Under these conditions hydrogen is absorbed, with the formation of a considerable proportion of stearic acid and other substances of higher melting-point, and the process is repeated until about 20-30% of the oleic acid has been converted. The solid products are then separated by chilling and filtering the mixture.

Better yields were obtained in Boehringer's process (G.P. 187788, 189332, 1906) in which the cathodes consisted of platinum coated with a layer of spongy platinum, or palladium coated with palladium black.

These methods are of historic, rather than practical, interest and their application on a commercial scale has not achieved notable or lasting success, later catalytic methods having proved to be superior. Recently, however, attention has again been directed to methods of converting olein to elaidin or other *iso*oleins as a means of hardening oils. A process of S. H. Bertram (Öle, Fette, Wachse, Seife, Kosmetik, 1938, No. 7, 1-4) claims that the conversion may be accomplished by means of 0.1-1% of selenium at 150-240°C. with formation of a product of satisfactory colour.

#### DEVELOPMENT OF HYDROGENATION PROCESSES.

The modern methods of catalytic hydrogenation are based on the investigations of Sabatier and Senderens, who showed that the unsaturated bonds in organic compounds could be made to combine with hydrogen by passing a mixture

of gases, e.g. ethylene or acetylene mixed with hydrogen, over heated finely divided nickel; cobalt, iron and platinum were less effective (Compt. rend. 1897, 124, 1358; 1899, 128, 1173; 1900, 130, 1628, 1761; 131, 40, 187).

A German patent for the hydrogenation of oils on these lines was taken out in 1902 by LePrince and Siveke, G.P. 141029, whilst in 1903 Normann (B.P. 1515, 1903) claimed a process of catalytically hydrogenating oils either in the form of vapour or as liquid. He stated, for example, that by suspending nickel powder in oleic acid heated in an oil bath, and passing a current of hydrogen, or of a gaseous mixture rich in hydrogen, through the liquid, the oleic acid could be completely converted into stearic acid.

Sabatier (Ann. Chim. Phys. 1909, [viii], 16, 73) converted oleic acid vapour into stearic acid by means of hydrogen and nickel, but believed that the vapour state was necessary for the reaction.

Successful technical hydrogenation of fats dates from the Normann patent. As was inevitable many difficulties were encountered in developing the method and it was not until the process was acquired by Joseph Crosfield & Sons of Warrington that it became, with Dr. Normann's assistance, a practical success. By 1910 several hundred tons of hardened oil were being produced per week and the process enabled substitutes to be produced at a price between £10 and £20 a ton cheaper than tallow. Economic changes, however, have affected the position considerably and it may now be said that the development of hydrogenation and the consequent increase in production of whale oil have caused the value of almost all edible oils to depend mainly on the value of whale oil.

The development of hydrogenation may be traced from the following account of some of the more important processes which have been patented since 1903.

An exhaustive account of these and other processes, and indeed of everything connected with oil-hardening, will be found in C. Ellis, "The Hydrogenation of Organic Substances, including Fats and Fuels," 3rd ed., D. van Nostrand Co., New York, 1930.

In Day's process (U.S.P. 826089, 1906) catalytic hydrogenation of hydrocarbon oils is employed to effect deodorisation, palladium black being used preferably as the catalyst.

Treatment of hydrocarbon oils by catalytic hydrogenation is now carried out on a large scale to produce greater proportions of valuable fractions from mineral oils. Complex mixtures of oxides and sulphides of various metals are employed as catalysts, and the reaction is conducted at high temperatures and pressures (v. HYDROGENATION OF COAL).

An apparatus claimed by Schwoerer (G.P. 199909, 1906) consists of a vessel containing a helical trough the underside of which is coated with asbestos impregnated with nickel. The oily substance, e.g. oleic acid, is brought into a fine state of division by means of superheated steam, and passed, together with hydrogen, into the vessel, where the mixture is heated to 250–270°. Under these conditions the hydrogen is absorbed, and the stearic acid deposited

to a large extent in the trough. Bedford and Williams' process (B.P. 9112, 1908) is concerned with the hydrogenation of oleic acid in the form of spray, the mixture of acid and hydrogen passing through two separate layers of catalytic material in a vertical tower, the internal temperature of which is maintained at about 200°. The reduction is carried out under ordinary pressure, vacuum is then applied and the product distilled over into a receiver connected to the tower.

In his processes described in G.P. 211669, 1907, 221890, 1909, Erdmann claims a method of hydrogenating oils in the form of a fine spray in presence of a nickel or other catalyst. Thus the oil may be finely divided by means of a jet of hydrogen in a chamber containing a rotating cylinder covered with a layer of the catalytic agent, and is then made to pass through a bed of pumice impregnated with nickel. Or the oil may be introduced as a spray into a tower nearly filled with porous catalytic material, and there meet a current of hydrogen from another inlet, the temperature being maintained at 170–180°. The solid product is preferably purified by treatment with steam under reduced pressure.

In the Kayser process, which is stated to be employed on a large scale in the United States, an inert powder such as kieselguhr is used as the carrier for a nickel catalyst, the oil being agitated with this at about 150–160°. One form of apparatus, used for effecting an intimate admixture of oil and catalyst, consists of a horizontal cylinder in which revolves a paddle wheel the skeleton blades of which are covered with wire gauze. Hydrogen under pressure is introduced at one end of the cylinder, and the unabsorbed gas is drawn off at the other end.

Hydrogenation under pressure is also a feature of Testrup's process (B.P. 7726, 1910), the mixture of finely divided oil and catalyst being pumped into a vessel containing an atmosphere of hydrogen. For example, a mixture of oil and palladium, or preferably nickel, may be heated to about 160° in a jacketed chamber, containing hydrogen under 12 atm. provided with a stirring device, and then forced through spraying nozzles into a second chamber, where the temperature is maintained at about 160–170°, and in which a hydrogen pressure of 9 atm. is maintained. If still harder products are required, the process may be repeated in another chamber into which hydrogen is admitted at a pressure lower by 3 atm., or a whole series of connected vessels may be used.

The use of autoclaves for hydrogenating oils has the advantage that the conversion is effected at a relatively low temperature (100–160°) thus obviating the risk of injury by overheating. In Wilbuschewitsch's process (F.P. 426343, 1910) an intimate mixture of the oil and catalyst is pumped or injected into a series of connected autoclaves, through which circulates a current of hydrogen in the opposite direction. The gas may be admitted in such a way that it disperses, in the form of a spray, the oily mixture accumulating in the bottom of the vessel, which is pumped into connected autoclaves, where the process is repeated until the product has the desired melting-point; or the



hydrogen passes counter-current through reducing valves into successive autoclaves with corresponding diminution of pressure.

In the process claimed by Bedford and Williams (B.P. 29612, 1910) about 1% of a metal oxide catalyst is added to the oil, which is heated by means of a steam coil, in a closed vessel, to about 250°, while hydrogen is introduced through a perforated pipe at the bottom of the vessel. By using a mixture of hydrogen and oxygen in place of pure hydrogen, hydroxy-fatty acids, or their compounds, may be produced by this process.

In order to effect the hydrogenation in stages at different temperatures Ellis has devised a method whereby the mixture of oil and metal catalyst is made to pass in a continuous stream through a long tube divided into a series of compartments, and encounters a current of hydrogen travelling in the opposite direction. Different temperatures are maintained in the different compartments, *e.g.* 150° in the first, 165° in the second, and 180° in the last (B.P. 24084, 1912). In Pietet's process (F.P. 472080, 1913) the oil, with or without the addition of a catalyst, is made to pass by gravitation through a series of communicating tubes, the walls of which are composed of catalytic metal. Hydrogen is introduced under suitable pressure, and the oil is finely divided and brought into intimate contact with the gas by means of rotating devices which brush continually against the walls of the tubes.

In order to obtain a large surface of catalytic material Dewar and Liebmann (B.P. 15668, 1914) distribute the catalyst over fibrous material such as yarn, which for strength may be enclosed between sheets of wire gauze. Or the fibrous material may be supported on frames attached to the agitator, or wound round the blades of the agitator in the hydrogenating apparatus.

In Calvert's hydrogenation process the oil is mixed with the catalyst and treated with hydrogen in a closed vessel containing a comb-shaped rotating agitator to subdivide the oil, whilst a centrifugal propeller at the base flings the mixture upwards to be beaten again (B.P. 5967, 1914).

The method of effecting minute subdivision of the oil adopted by Moore (U.S.P. 1121860, 1914) is to pass it together with the hydrogen through catalytic material which may be contained in a diaphragm porous to the oil and gas, but not to the catalyst.

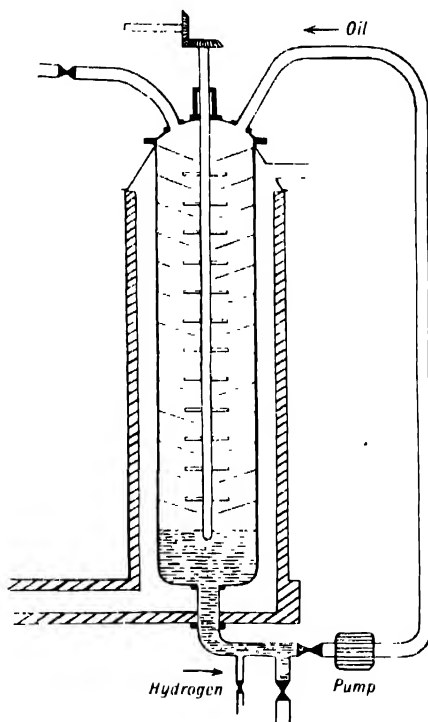
Lane's apparatus (B.P. 968, 1915) consists of a vertical cylindrical vessel which is heated by means of a steam jacket or otherwise. Beaters rotating horizontally round a central shaft alternate with annular sloping shelves on the sides of the vessel, so that the oil and catalyst, entering at the top, are alternately sprayed outwards to the sides and guided to the centre of the beaters next below; and so on, until they reach the bottom and are then pumped again to the top. The hydrogen enters by a pipe at the base of the apparatus.

In Walker's process (U.S.P. 1123962, 1915) the melted fatty acids or glycerides are sprayed against

heated, finely divided, catalytic material, in presence of an electric discharge.

The essential features of the process of Birkenland and Devik (U.S.P. 1125259, 1915) are that the oil is mixed with the catalyst and a portion forced from a jet into an atmosphere of hydrogen, and thence downwards into the body of the oil, whereby hydrogen is conveyed by suction to the bottom of the vessel and is absorbed on rising through the oil.

McElroy (U.S.P. 1157903, 1915) claims the use of an emulsifying process. Freshly reduced nickel is mixed with the oil, and hydrogen is made to circulate through the liquid in minute ascending bubbles in a special form of apparatus, in such a way as to produce a gas-liquid emulsion.



LANE'S APPARATUS.

The apparatus devised by Maxted and Riddale (B.P. 109903, 1916) consists of a vertical column provided with baffle plates, so arranged that a mixture of oil, catalyst and hydrogen, projected into the top of the vessel, is rotated alternately first in one direction and then in the other on its passage to the bottom.

The essential feature of the process of Wells (U.S.P. 1383887, 1921) is the vigorous agitation of the reaction mixture by the introduction of a stream of hydrogen from beneath.

In the apparatus described by Mellersh-Jackson (B.P. 175021, 1920), hydrogen is admitted through a distributing plate of porous material and rises in uniform bubbles through the oil. In another type of apparatus (Ellis, U.S.P. 1480251,

1924) the oil is made to circulate in vertical planes in a long horizontal cylindrical tank by means of convection currents produced by heating coils placed in suitable positions. In another patent, also of Ellis (U.S.P. 1476330, 1923), the hydrogen is made to bubble through the oil at 150–200°, and is arrested by the nickel catalyst which is contained in a finely divided powder of inert material.

A new type of apparatus and process is claimed by Ruben (U.S.P. 1554296, 1925), in which a liquid with a high dielectric constant is passed upwards through a metal cylinder, containing a suspended porous pot with a dielectric constant lower than that of the liquid under treatment. This pot, which has a conductive inner surface, is supplied with a high frequency alternating current of high potential, whilst the conductive wall of the outer cylinder is connected with the other pole. Under these conditions hydrogenation of the oil is effected without the use of a catalyst.

In B.P. 341153, 1929, claim is made by the I.G. Farbenind. A.-G. for resistant zinc alloys, m.p. above 500°, for constructing or lining the hydrogenation vessels and connections.

In 1922 E. R. Bolton (J.S.C.I. 1922, 41, 384R) noted that the technical application of an apparently simple catalytic reaction had already inspired the subject-matter of 300 patents. This number has been largely increased since, and it may be said that the processes now in operation are all based on the fundamental concept of Sabatier-Senderens and differ only in method of catalyst production, mechanical details of admixture of oil, catalyst and hydrogen; reaction conditions of temperature and pressure, and after-treatment of products. A comparatively small weight of hydrogen is required (less than 0.7% by weight) but its volume is such that the efficiency of the process necessarily depends largely on the degree of admixture of the reactants with the catalyst and on the efficiency of the latter.

#### CATALYSTS FOR HYDROGENATION.

In the original investigations on catalytic hydrogenation by Sabatier and Senderens finely divided platinum or palladium was used as the catalytic agent, but as nickel is a much less expensive catalyst than those metals it is now almost universally employed for the hydrogenation of oils and fats. The use of other metals such as palladium, cobalt, iron and copper as catalytic agents has also been claimed in several of the patent processes of hydrogenation.

In preparing a nickel catalyst the usual method is to precipitate nickel hydroxide or carbonate from a solution of a salt such as nickel sulphate, in the presence of inert material such as kieselguhr, to dry the sludge and to reduce it in a current of hydrogen at a temperature of 300–325°.

In Lane's process (Engineer, 1917, 123, 511) solutions of nickel sulphate and of sodium carbonate are prepared in separate tanks provided with steam jets, and are transferred into a third tank provided with a mixing apparatus and containing inert support-material, such as kieselguhr. The mixture of precipitated nickel

carbonate and kieselguhr is dried, ground and roasted to convert the carbonate into oxide, after which it is heated in a current of hydrogen.

One form of apparatus used for this purpose is a vertical vessel provided with external means of heating, and containing a series of reciprocating grids. The powdered material is introduced at the top and falls on to the successive grids, the movement of which exposes fresh particles to the current of hydrogen, which is admitted at the base, and rises through the grids to the outlet at the top of the apparatus. The reduced material falls into a vessel containing oil of the same kind as is to be hydrogenated, and, after being thoroughly mixed, the oily mass is ground until of the desired consistency.

The method of preparing the catalyst has a considerable influence on its activity and its resistance to external influences. For example, nickel which has been reduced at as low a temperature as possible is more effective than that reduced at a higher temperature, but, on the other hand, is also more sensitive to the action of catalyst "poisons." Ellis (J.S.C.I. 1912, 31, 1163) gives 300–325° as a suitable temperature for the reduction. According to Kelber, however (Ber. 1916, 49, 1868), a catalyst prepared by reducing basic nickel carbonate with hydrogen at 450° is more sensitive to poisons than one prepared at 310°. On the other hand a catalytic agent prepared by reducing the basic carbonate on Florida earth (Kelber, *l.c.*, p. 60) at 450° proved remarkably resistant to the action of hydrocyanic acid, hydrogen sulphide and carbon disulphide.

Nickel catalysts may be prepared from carbonates and oxides of the metal by reduction at temperatures as low as 150°C. and will remain active in use for long periods with suitable oils.

The activity of a catalyst has also some determining effect on the nature of the reaction, suppressing or promoting the formation of isomeric glycerides of oleic acid which always accompanies hydrogenation of unsaturated fatty oils. M. G. Barradas (U.S.P. 2014999, 1935) claims to control the selectivity of hydrogenation by admixing various proportions of an inert gas with the hydrogen used.

Reduced iron, sodium chloride, sodium sulphate and sodium nitrate have no influence on the activity of nickel catalysts, but sodium sulphide gradually impairs the efficiency, and sulphur destroys it immediately (Moore, Richter and Van Arsdell, *Ind. Eng. Chem.* 1917, 9, 451). Nickel may also be rendered inactive by traces of chlorine and of decomposition products in the oils undergoing hydrogenation. For this reason low-grade oils, such as whale and fish oils, may speedily render a nickel catalyst inactive. Heating and agitating the oil with freshly-precipitated copper hydroxide has been found an effective means of removing the poisonous constituents from such oils, especially after a preliminary treatment with sodium carbonate solution (Ellis and Wells, *ibid.* 1916, 8, 886). In some cases, however, it is necessary to hydrogenate the oil in two stages, filtering off the catalyst after it has become inactive. Veno (J. Chem. Ind. Tokyo, 1918, 21, 898) has shown that powdered metals (not

reduced by hydrogen), such as nickel, tin, zirconium and copper, have but little injurious action on catalytic hydrogenation, but that iron, zinc, lead and mercury act as poisons.

For a detailed study of the effect of various catalyst poisons on platinum, see Maxted (J.C.S. 1925, 127, 73; 1928, 1600; 1931, 2203).

Catalysts resistant to poisoning by sulphur are prepared, according to B.P. 415203/1923 of I.G. Farbenind. A.-G., in the form of sulphides of the heavy metals of groups V and VI and Fe, Ni, Co. The best results are obtained with Mo or W sulphides singly or as a mixture.

The efficiency of a catalytic metal, being at any rate partly determined by the extent of its surface, is considerably increased by distributing it over a porous non-catalytic support such as charcoal, powdered pumice or kieselguhr, and the method of impregnating the support with the metal forms the subject-matter of numerous patents. In Crosfield's process (B.P. 30282, 1910) an inert medium, such as asbestos or kieselguhr, is impregnated with a solution of nickel sulphate, and then treated with a solution of an alkali hydroxide. The mass, which now contains nickel hydroxide, is washed, dried and heated in a current of hydrogen; and the resulting product should contain about 30% of metallic nickel.

Kayser (U.S.P. 1004034, 1911) saturates the porous support with a solution of a nickel salt, and incorporates therewith molecular proportions of powdered sodium carbonate. The mixture is then treated with boiling water, dried and the nickel salt reduced. In a later patent (U.S.P. 1001279, 1911) Kayser claims a method of preparing a catalyst which may be exposed to the air for several days without undergoing oxidation and losing its catalytic activity. In this process nickel oxide is reduced at about 500–600°, and a current of carbon dioxide passed through the material until the gas leaving the apparatus is no longer inflammable.

In Bolton and Lush's process (B.P. 162382, 1920) the poisoning of the catalyst through the formation of nickel soap is prevented by adding mono- or diglycerides to the oil. These combine with any free fatty acids present and so prevent the nickel being attacked. Bolton has also claimed a method of restoring the activity of the catalyst by washing it in the apparatus, first with hot oil to remove soap and then with a solvent to remove the oil (B.P. 162370, 1920).

Lessing (B.P. 18998, 1912) claims the use of a catalyst composed of nickel carbonyl or other metallic compound which undergoes decomposition at the temperature of hydrogenation.

Reduction of nickel formate in the oil itself is described in a process of Brochet (Bull. Soc. chim. 1920, [iv], 27, 899). Processes based on this method have acquired considerable technical importance.

Bedford and Erdmann (B.P. 27718, 1912) make use of metallic oxides in a form suitable for catalytic agents. They assert (J. pr. Chem. 1913, [ii], 87, 425) that nickel oxides are much less sensitive than metallic nickel to external influences, and that they effect more rapid hydrogenation. The activity of the catalytic agent is increased by the presence of the

oxides of other metals. In carrying out the process the oil is heated to 180° in a cylindrical copper vessel fitted with an agitator, while a slow current of hydrogen is passed through it. A small quantity of nickel oxide is introduced, the temperature raised to 255–260°, and, after the addition of more catalyst, the supply of hydrogen is increased. It is claimed that the hydrogenated product is free from hydroxy-acids, and that nickel soap is formed only to a very limited extent.

Erdmann and Rack attribute any activity of nickel borate to the formation of nickel oxides at 260°. Contrary to the claim of Schönfeld, they find that nickel borate does not convey hydrogen to unsaturated fats at 175°. Normann, however, attributes the catalytic activity of nickel borate to the formation of metallic nickel produced by the hydrogen during the hydrogenation process, and finds that there is no positive evidence of the presence of nickel suboxide.

Meigen's experiments (J. pr. Chem. 1915, [ii], 92, 390) are opposed to the view of Erdmann and Bedford, that an oxide or suboxide of nickel is the catalytic agent. He concludes that while it is conceivable that their view may be correct, it is a hypothesis which is lacking in experimental proof.

In Byron's method of preparing a stable catalyst (B.P. 13382, 1913) the solution of a salt of a catalytically active metal, such as nickel sulphate, is treated with a solution of an alkali silicate, and the precipitate dried, and, if desired, reduced in a current of hydrogen.

Richardson (U.S.P. 1151718, 1915) claims the use of an oleate of nickel or other metal; whilst Bacon and Nicolet (U.S.P. 1152591, 1915) prepare a catalyst containing nickel hydroxide and aluminium hydroxide, in which the nickel has been rendered active by reduction with hydrogen. Catalysts composed of aluminates of nickel or other heavy metals have also been patented by De Nordiske Fabriker De-No-Fa A/s. (B.P. 140371, 1919).

Catalysts are prepared by Raney (U.S.P. 1628190, 1927) by alloying nickel and aluminium and submitting the alloy to the action of alkali. The resulting material having a cellular micro-structure is of a very active nature and has been much employed—chiefly in research—under the name of "*Raney nickel*." If the action of the alkali is restricted to the surface of turnings of the alloy the catalyst may be used in massive form, thus leaving only traces of metal to be removed from the oil after hydrogenation.

L. G. Jenness (Oil and Soap, 1934, 11, 131) prepares "*foraminite*" catalysts by selective corrosion of aggregates of the catalytic metal and other material, claiming such catalysts to be of superior activity.

A catalytic agent claimed by Ellis (U.S.P. 1158068) is prepared by incorporating hydrated nickel hydroxide,  $\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , with an oily medium, reducing the nickel compound with hydrogen, and removing moisture from the product. In another process, also patented by Ellis (U.S.P. 1159480, 1915), a basic compound of nickel is partly reduced with hydrogen to

obtain a catalyst consisting of nickel and a lower oxide of nickel.

Catalysts described by Ellis (U.S.P. 1378336-7-8, 1921) are prepared by incorporating organic salts of nickel, etc., with an oily medium, and heating the mixture at reduced pressure, *e.g.* heating nickel oleate in the presence of non-reducing inert gases; and by reducing mixtures of metallic salts of nickel, copper and cobalt in an oily medium.

Armstrong and Hilditch (Proc. Roy. Soc. 1922, A, 102, 27) investigated the influence of copper in promoting the activity of a nickel catalyst. They found that a lower temperature (180°) was required for the reduction, whereas the nickel compound by itself was not reduced by hydrogen below 300°. Grote (Seifens.-Ztg. 1920, 47, 713) found that by using a catalyst consisting of a colloidal double nickel and magnesium (or aluminium) silicate, dried and reduced in hydrogen, the time of hydrogenation could be reduced to 10 minutes and the temperature to 160°. The addition of a phenolic substance (quinol, guaiacol or resorcinol) is claimed to accelerate hydrogenation (Lever Bros., Ltd., and R. Thomas, B.P. 208189, 1922).

Metallic soaps and other impurities which act as "poisons" to the catalyst may be removed by treatment with Japanese fuller's earth (S. Ueno, J. Soc. Chem. Ind. Japan, 1920, 23, 1028).

#### CONTINUOUS PROCESSES.

A series of processes were devised for the continuous hydrogenation of oils by Bolton and co-workers from 1920 onwards in which the catalyst is used in massive form and oil is passed over it at suitable temperatures in an atmosphere of hydrogen. Thus E. R. Bolton (B.P. 162370, 1920) activates nickel wool by treating it with nitric acid in liquid or vapour form, then roasting it and reducing adhering oxides with hydrogen. Oil and hydrogen are passed in counter-current over the catalyst which may be reactivated by treatment with hot oil and solvents.

A great advance was made by the introduction of Bolton and Lush's continuous process (Lush and Technical Research Works, Ltd., B.P. 203218, 1922), which is successfully worked in many countries by licences from Technical Research Works, Ltd. The catalyst consists of nickel wire or turnings enclosed in cages of metallic gauze. The cage and its contents are coated with a film of nickel peroxide in an electrolytic bath, with the cage itself as the anode, whilst a 5% solution of sodium carbonate forms the electrolyte. The cages are inserted into the apparatus and the nickel peroxide is reduced to nickel by means of a current of hydrogen at 200-250°, after which the temperature is allowed to fall to 180°, and the oil is made to flow over the catalyst. When the catalyst becomes inactive (after periods up to 6 months) the residual oil is extracted from the cages *in situ*, the solvent is removed, and the cages and their contents are re-activated by anodic oxidation in the electrolytic bath and returned to the plant for further use. A

description of the plant on an industrial scale is given by Lush (Ind. Chem. 1927, 3, 249). Manderstam (Oil and Soap, 1939, 16, 166) deals with later developments. In addition to the advantage of the process being continuous, it is claimed that there is no hydrolysis of the oil, that the period of initial heating is short, and that the cost of production is lower than in the older powder processes.

Reference may also be made to the "T.R.W. Interchange Process," in which a saturated body (*e.g.* butyl alcohol) is mixed with an unsaturated body (*e.g.* olein), and the mixture is passed over the catalyst under conditions similar to those employed for direct hydrogenation. Hydrogen is transferred from one body to the other, with the formation of *e.g.* butaldehyde and stearin. According to the patent of Technical Research Works and Lush (B.P. 221000, 1923) the spent catalyst is freed from oil, and is then oxidised at the surface with hypochlorous acid and reduced with hydrogen.

#### HYDROGEN FOR CATALYTIC PROCESSES.

One of the main essentials for the successful hydrogenation of oils is a supply of pure hydrogen. The gas must be free from sulphur, chlorine, arsenic and phosphorus, and contain only negligible quantities of oxygen or oxides of carbon.

In some of the larger works (Siemens-Schuckert, Ateliers Oerlikon) a very pure hydrogen, containing as impurity only 0.2% of oxygen, is prepared by the electrolysis of alkaline distilled water. In other works water gas or producer gas is used as the source of hydrogen. The methods of Linde-Frank-Caro and of the Soc. de l'Air Liquide are based on a fractional distillation of the liquefied components of water gas. The resulting hydrogen is of 97-98% purity, and is brought to 99.995% by being passed over soda-lime heated to 180°.

In Lanc's process (Anon., Engineering, 1917, 123, 546) steam is decomposed by means of reduced iron, and the resulting iron oxide is reduced by purified water gas. Spathic iron ore (ferrous carbonate) is used as the original source of iron. This, when heated, yields a porous mass of ferrous oxide, which is packed into a retort, where it is alternately reduced and oxidised. The cost of hydrogen made by this process was about 4s. 2d. per 1,000 cu. ft. (Elhs, J.S.C.I. 1912, 31, 1164). A mixture of steam and water gas is used by the Soc. Lyonnaise du Gaz and the Griesheim-Elektron Co., the decomposition being effected by means of a mixture of lime and iron. These methods yield hydrogen of 97.5-98.5% purity.

Where petroleum is readily obtainable the method of Rincker-Wolter is used, in which the hydrocarbons of oil gas are decomposed at a high temperature into carbon and hydrogen.

Electrolytic hydrogen is now largely used for catalytic hydrogenation, the processes and plant of Knowles (International Electrolytic Plant Co., Ltd.) and Bamag-Meguini A.-G. (Berlin) being widely used. The Knowles cell produces 8 cu. ft. per kw.-hour of hydrogen of 99.9%

purity at an economical voltage (E. F. Armstrong, Chem. and Ind. 1932, 61, 92).

#### TECHNOLOGY OF HYDROGENATION.

From a consideration of the foregoing outlines of patent processes it will be seen that the main conditions for successful hydrogenation are a suitable temperature, fine state of subdivision of the oil, an active catalyst and the absence of injurious substances.

E. F. Armstrong and K. A. Williams (Chim. et Ind. 1939, 42, 2; Chem. and Ind. 1940, 59, 3) point out that the technology of hydrogenation has now advanced to a stage where the older processes have all become more or less standardised in operation. The many difficulties encountered in the early development have mostly been eliminated, so that while in 1910 several hundred tons of oil were treated per week, the output of hydrogenation plant had risen by 1939 to the order of 1,000 tons per day and the process had become applied to many substances other than fatty oils. Chemicals, such as phenol, cresols, naphthalene and pyridine, are treated in limited quantities, while with coal and petroleum oils the industry is conducted on an enormous scale.

In order to avoid catalyst poisoning extremely careful refining of fatty oils is necessary before they are hardened.

"Powder" or "batch" processes are applied in autoclaves, the nickel catalyst usually being prepared by suspending an inert carrier in a solution of nickel sulphate to which is added sodium carbonate. The precipitate is thoroughly washed and dried, and reduced in a current of hydrogen at 250°C. or more, according to the degree of activity required, the temperature used affecting also the robustness. After cooling the catalyst is flooded with oil and stored until required. Hydrogenation is conducted in autoclaves at about 180°C. in an atmosphere of hydrogen, under pressures in excess of atmospheric. The reaction occurs at a rate that can readily be controlled, and a rapid examination of the product at intervals enables the reaction to be stopped at any desired stage.

Nickel formate catalyst is also used, with or without support, in a similar manner and is reduced *in situ* in the oil at about 250°C., saving plant, labour, and operating costs by combining the catalyst reduction and hydrogenation processes.

In batch processes, the oil is cooled and the catalyst filtered off after the reaction has proceeded far enough. The oil generally requires further refining and bleaching and will almost always require deodorising.

The "continuous" system of Technical Research Works, Ltd., is applied as described above, and in this case the hardened oil emerging from the plant contains less than 1 part of nickel per 10 million of oil. Subsequent filtration and refining are unnecessary but deodorisation is usually applied. In practice it has been found that the oil suffers from continual contact with the heated walls of the vessel, and the short time of contact of oil, hydrogen and catalyst employed in this system is therefore advantageous.

It is believed that with oils, such as whale oil, cotton-seed and ground-nut oils, the powder systems involve running costs of from 25s. to 30s. per ton and the continuous system of about one-half this sum. The latter system requires less labour and floor-space.

Fatty alcohols are now produced on a large scale by catalytic hydrogenation of oils or fatty acids under very high pressures, such conditions promoting the reduction of the carbonyl group. The products find use after sulphonation as wetting agents.

#### PROPERTIES OF HYDROGENATED OILS.

The degree of hardening depends upon the extent to which the hydrogenation process has been carried, so that products ranging from the consistence of a soft butter to a hard tallow may be obtained from the same oil.

Provided that the reaction is carried far enough, fish oils and whale oils are deodorised during hydrogenation owing to the conversion of the clupanodonic acid (to which, as Tsujimoto has shown, the odour is mainly due).

For edible purposes the chief oils hydrogenated are whale oil, cotton-seed, maize, soya bean, arachis and coconut oils, though any edible oil is suitable for the process. Products such as margarine and artificial lard, which formerly consisted of a vegetable oil mixed with sufficient oleostearin to give a semi-solid mass, are now prepared from oils such as cotton-seed oil or whale oil hydrogenated to a sufficient extent to give the required consistence; or by a mixture of hardened oils with liquid oils. In the opinion of Ellis (J.S.C.I. 1912, 31, 1165) the use of hydrogenated oils by themselves is preferable to the method of some manufacturers of blending hydrogenated oils with untreated oils, since the resulting product has a better flavour and keeps better.

With regard to the effect of hydrogenation on oils it has been found that the acid and saponification values are not materially affected, but the refractive index and iodine value are lowered and the melting-point raised to an extent corresponding with the degree of hydrogenation.

The acetyl value of hydroxylated oils such as castor oil is lowered by hydrogenation at the usual temperatures, but Jurgens and Meigen have shown that when esters of ricinoleic acid are hydrogenated below 200° the OH group is not attacked and practically only the double bond is saturated.

While the catalytic hydrogenation of many chemicals consists in the simple addition of hydrogen at the double bonds, in some cases there is preferential action. If a compound contains more than one double bond all may react but more generally the reaction is limited to specific bonds. Thus E. J. Lush (J.S.C.I. 1927, 46, 454) has shown naphthalene to produce tetralin if treated in the vapour phase and decalin when in the liquid phase. Unsaturation in aromatic nuclei is generally less easily removed than in straight chains, and in a straight chain containing two or more double bonds one will be more readily reduced than another.

E. F. Armstrong and K. A. Williams (Chim. et Ind. 1939, **42**, No. 2, 234) point out that fatty oils consist of complex mixtures of glyceryl esters of fatty acids. The fatty acids are all of similar chain length but may be saturated, or contain one, two, three or more double bonds. Three acid radicals are attached to each glyceryl radical in a manner even now incompletely understood, though T. P. Hilditch and his co-workers continue to throw light on the problem. It is not known how the arrangement of the acids on the glyceryl residue affects the relative ease of reduction but it is believed that this has little effect in most cases. R. G. Pelly (J.S.C.I. 1927, **46**, 449r) has shown, however, that in mixtures of fatty acids and neutral fats the unsaturated free acids are preferentially reduced. Further complications occur through side-reactions. There is a notable formation of isomers of oleic acid in batch hydrogenation; this can be largely suppressed in the continuous process.

Experiments on the hydrogenation of cotton-seed oil by Moore, Richter and Van Arsdel (Ind. Eng. Chem. 1917, **9**, 451) have shown that linolein is hydrogenated more rapidly than olein at 200° and upwards, so that olein tends to accumulate in the fat. To obtain a hardened product with the same iodine value as another but containing, relatively, more saturated glycerides and linolein, it is necessary to effect the hydrogenation under conditions of lower temperature, greater pressure, more vigorous agitation and a larger proportion of catalyst.

It was found by E. F. Armstrong and T. P. Hilditch (Proc. Roy. Soc. 1920, A, **98**, 27) that in the hydrogenation of linseed oil in the presence of a nickel catalyst, a curve results the initial portion of which (30% of the whole curve) corresponds with the hydrogenation of the whole of the linolenin and most of the linolein; there is then a very abrupt change in the curve, and this is followed by an approximately linear curve at a much lower slope.

In a further communication by the same authors (*ibid.* 1921, A, **100**, 240) on the influence of pressure on the hydrogenation of liquids in the presence of nickel, it was shown that, in the absence of disturbing factors, an increase in the pressure of the hydrogen causes a proportionate increase in the rate of reduction. According to Lush (J.S.C.I. 1924, **43**, 53r), the rate of hydrogenation is approximately proportional to the square root of the pressure.

Varying the mass of oil in relation to the catalyst has a pronounced effect on the nature of the products, and hydrogenated oils containing different proportions of isooleic acid may thus be obtained (Lush, *ibid.* 1923, **42**, 219r). The influence of the concentration of the catalyst on the selective hydrogenation of cotton-seed oil has also been studied by Dhingra, Hilditch and Rhead (J.S.C.I. 1932, **51**, 195r); see also E. R. Bolton, *ibid.* 1927, **46**, 44r, and "Oils, Fats, and Fatty Foods," 1928, pp. 302-316.

R. Thomas (J.S.C.I. 1920, **39**, 10r), studying different aspects of the mechanism of the hydrogenation of unsaturated glycerides in the presence of a nickel catalyst, found that the

influence of foreign gases on the catalyst and on the velocity of hydrogenation might be either purely physical or chemical. He confirmed the observation of Armstrong and Hilditch that linolein absorbs hydrogen much more rapidly than does olein. Kaufmann's thiocyanogen method of determining the degree of unsaturation of fats has also afforded proof of the selective character of hydrogenation (Kaufmann and Hansen-Schmidt, Ber. 1927, **60** [13], 50). In experiments with a nickel catalyst at 200° in an autoclave the linoleic acid in a fat had disappeared after 135 minutes.

The effects of the temperature of hydrogenation on the selective action and upon the melting-point and iodine value of the product have been studied by K. A. Williams (J.S.C.I. 1927, **46**, 446r, 448r) over a range of 120-200°.

The formation of isooleic acid is dealt with by Moore (*ibid.* 1919, **38**, 320r); Hilditch and Moore (*ibid.* 1923, **42**, 15r); Richardson, Knuth and Milligan (Ind. Eng. Chem. 1924, **16**, 519; 1925, **17**, 80) Cocks, Christian and Harding (Analyst, 1932, **56**, 368); Lush (J.S.C.I. 1923, **42**, 219r; 1924, **43**, 53r; 1925, **44**, 129r); Hilditch and Vidyarthi (Proc. Roy. Soc. 1929, A, **122**, 552).

Elaidic acid is the predominating isomer formed but a number of others also appear. The total proportion of isomers formed depends on temperature, possibly on pressure, certainly on the degree of activity of the catalyst, the relative degree of mixing of oil and catalyst, the rapidity of desorption of reacting molecules from the catalyst and the nature of the catalyst.

It is most marked with platinum, less with palladium, still less with nickel and least with copper. It is promoted by high temperatures and is least marked in the continuous process. Under constant conditions, the ratio of solid isooleic acid to liquid oleic acid in the product tends to a constant value after the reaction has proceeded to a fixed extent, this value being maintained until saturation is complete. Unpublished researches of K. A. Williams suggest that the proportions and the reactions themselves are controlled by excess electronic energy acquired by hydrogen in its sorption by the catalytic metal and subsequent transfer to the oil molecule.

The theory of the catalytic action is dealt with by Rideal and Taylor, "Catalysis in Theory and Practice," 1926; Falk, "Catalytic Action," 1922; Sabatier, "Le Catalyse en Chimie Organique," 1920; various reports of the American Committee on Contact Catalysis, 1922-26; Nyrop, "Treatise on the Catalytic Action of Surfaces," Copenhagen, 1934; Hilditch, "Catalytic Processes in Applied Chemistry," 1929; H. S. Taylor (Proc. Roy. Soc. 1925, A, **108**, 105; J. Phys. Chem. 1926, **30**, 150); Joelen (Fettchem. Umschau, 1934, **41**, 95, 51); Berkman, Morrell and Egloff, "Catalysis," Reinhold Publishing Co., New York, 1940, hydrogenation, pp. 809-887.

Arachidic acid may still be detected in hardened arachis oil, but a modification of the usual test is necessary (see Kreis and Roth, Z. Unters. Nahr.-u. Genussm. 1913, **25**, 81).

Leimdorfer (Chem. Zentr. 1914, I, 304) has shown that the stearic acid formed in the hydrogenation of oils is chemically identical with natural stearic acid.

Marine animal oils yield a much smaller proportion of insoluble bromides after hydrogenation, and the distinctive colour reactions of the original oils are either modified or no longer obtained.

Bellier's reagent (nitric acid, sp.gr. 1.4, and resorcinol in benzene) also gives different colour reactions with hardened sesamé, cotton-seed and arachis oils from those given by the original oils. The Baudouin test for sesamé oil is intensified by hydrogenation, but Halphen's test for cotton-seed oil is inhibited, the chromogenic substance giving the reaction being destroyed after hydrogenation for 15 minutes with a nickel catalyst at 150–160°.

The amount of phytosterol is not materially reduced by hydrogenation at 200°, but cholesterol is resimified at 200°, and after treatment at 250° will no longer yield a crystalline derivative (Marcussou and Meyerheim, Z. angew. Chem. 1914, 27, 201).

Analytical data for hydrogenated oils are given by Bomer and Leschly-Hansen (J.S.C.I. 1912, 31, 996); E. Mellana (*ibid.* 1914, 33, 701); Sudborough, Watson and Athawale (*ibid.* 1923, 42, 103A); Myddleton and Barry, "Fats Natural and Synthetic," E. Benn, Ltd., 1924; Williams and Bolton (Analyst, 1924, 49, 460); Williams (J.S.C.I. 1927, 46, 446, 448T); and in other communications already referred to.

The hydrogenation of tung oil is referred to by H. I. Waterman and C. van Vlodorp (Chem. Weekblad. 1934, 31, 420) who point out that the course of the reaction varies with temperature and pressure and with the nature of the catalyst. T. Moore (Biochem. J. 1839, 33, 1635) has found that the strong spectrographic absorption at 270 $\mu$  drops, while the originally small value at 230 $\mu$  first rises and then drops, both reaching negligible values at saturation. He compares the formation of an acid with absorption maximum at 230 $\mu$ , indicated by this observation, with the formation of the same acid by hens and rats fed on tung oil. He also notes that the hydrogen absorption and drop in iodine value do not correspond in the hydrogenation of tung oil, ascribing this discrepancy to the effect of conjugated bonds.

For a study of the alteration in glyceride structure produced during the progressive hydrogenation of olive and cotton-seed oils, see Williams and Bolton (Analyst, 1924, 49, 460) and Hilditch and Jones (J.C.S. 1932, 805); and for investigations of the course of hydrogenation in the continuous process of Technical Research Works, Ltd., see Lush (J.S.C.I. 1923, 42, 219T; 1924, 43, 53T); Hilditch and Rhead (J.S.C.I. 1932, 51, 198T). Williams and Bolton (Analyst, 1924, 49, 460) base a method for detecting hydrogenated oils on the determination of isooleic acid, using the insolubility of the lead salt of the latter in ether and alcohol as a means of separating it in admixture with saturated acids from the liquid acids. This test affords a much more trustworthy indication than the presence of nickel, which is now practically eliminated from

the products of hydrogenation. J. Grossfeld and J. Peter (Z. Unters. Lebensm. 1934, 68, 345) have extended the applicability of this test.

#### NICKEL IN HYDROGENATED FATS.

The presence of a trace of the metallic catalyst was at one time of frequent occurrence in hydrogenated fats, especially those of continental origin. Bömer (Chem. Rev. Fett.-u. Marz-Ind. 1912, 19, 221) found 0.01% of ash with 0.006% of nickel oxide in hydrogenated sesamé oil, and 0.006% of ash with 0.0045% of nickel oxide in hardened whale oil. Hence, the detection of nickel in a fat indicates the presence of a hardened oil, although a negative result in the test does not necessarily prove that such products are absent, since means, such as treatment with dilute hydrochloric acid, are often employed to remove the residual metal. In experiments to ascertain the effect of traces of nickel upon the human system, Offerdahl (Ber. deut. pharm. Ges. 1913, 23, 558) found that 0.5 g. of nickel could be taken daily without any injurious effect, 99.8% of the metal being rapidly excreted from the system.

Modern edible hydrogenated fats do not usually contain more than 1 part of nickel per 10 million and often much less.

For the detection of traces of nickel the dimethylglyoxime test may be used (*see* Knapp, Analyst, 1913, 38, 102), but certain untreated oils, free from nickel, may show a similar coloration if the test is made directly on the oil. The test should therefore be applied to the ash of 100 g. of the oil for better results (Prall, Z. angew. Chem. 1915, 28, i, 40). A still more sensitive reagent for nickel is a  $\alpha$ -benzildioxime, as suggested by Atack (Analyst, 1913, 38, 316).

To obtain products relatively free from nickel, Ellis (J.S.C.I. 1912, 31, 1165) lays stress upon the importance of using the catalyst in metallic form rather than in the form of oxide, since metallic nickel will not readily combine with free fatty acids to form a soap in the presence of free hydrogen. Too rapid hydrogenation should also be avoided, so as to prevent decomposition of the fat, with liberation of water, which might cause hydrolysis of the fat and liberation of free fatty acids.

For the mechanism of the addition of hydrogen to unsaturated glycerides in the presence of nickel, *see* Thomas (J.S.C.I. 1920, 39, 10T); and for a study of the relation between the occlusive power of palladium for hydrogen and its activity in catalytic hydrogenation, *see* Maxted (J.C.S. 1921, 119, 1281).

#### NUTRITIVE VALUE OF HARDENED OILS.

The digestibility of hydrogenated fats is dealt with by Langworthy (Ind. Eng. Chem. 1923, 15, 276) who describes researches of the U.S. Department of Agriculture. The conclusion is drawn that soft hydrogenated fats are as well assimilated as natural fats, but if the melting-point is raised beyond 40–45° the digestibility falls rapidly.

The food value of hydrogenated fats is much the same as that of natural fats, but commercial hardening processes almost always destroy any

E. F. Armstrong and K. A. Williams (Chim. et Ind. 1939, **42**, No. 2, 234) point out that fatty oils consist of complex mixtures of glyceryl esters of fatty acids. The fatty acids are all of similar chain length but may be saturated, or contain one, two, three or more double bonds. Three acid radicals are attached to each glyceryl radical in a manner even now incompletely understood, though T. P. Hilditch and his co-workers continue to throw light on the problem. It is not known how the arrangement of the acids on the glyceryl residue affects the relative ease of reduction but it is believed that this has little effect in most cases. R. G. Pelly (J.S.C.I. 1927, **46**, 449r) has shown, however, that in mixtures of fatty acids and neutral fats the unsaturated free acids are preferentially reduced. Further complications occur through side-reactions. There is a notable formation of isomers of oleic acid in batch hydrogenation; this can be largely suppressed in the continuous process.

Experiments on the hydrogenation of cotton-seed oil by Moore, Richter and Van Arsdel (Ind. Eng. Chem. 1917, **9**, 451) have shown that linolein is hydrogenated more rapidly than olein at 200° and upwards, so that olein tends to accumulate in the fat. To obtain a hardened product with the same iodine value as another but containing, relatively, more saturated glycerides and linolein, it is necessary to effect the hydrogenation under conditions of lower temperature, greater pressure, more vigorous agitation and a larger proportion of catalyst.

It was found by E. F. Armstrong and T. P. Hilditch (Proc. Roy. Soc. 1920, A, **98**, 27) that in the hydrogenation of linseed oil in the presence of a nickel catalyst, a curve results the initial portion of which (30% of the whole curve) corresponds with the hydrogenation of the whole of the linolenin and most of the linolein; there is then a very abrupt change in the curve, and this is followed by an approximately linear curve at a much lower slope.

In a further communication by the same authors (*ibid.* 1921, A, **100**, 240) on the influence of pressure on the hydrogenation of liquids in the presence of nickel, it was shown that, in the absence of disturbing factors, an increase in the pressure of the hydrogen causes a proportionate increase in the rate of reduction. According to Lush (J.S.C.I. 1924, **43**, 53r), the rate of hydrogenation is approximately proportional to the square root of the pressure.

Varying the mass of oil in relation to the catalyst has a pronounced effect on the nature of the products, and hydrogenated oils containing different proportions of isooleic acid may thus be obtained (Lush, *ibid.* 1923, **42**, 219r). The influence of the concentration of the catalyst on the selective hydrogenation of cotton-seed oil has also been studied by Dhingra, Hilditch and Rhead (J.S.C.I. 1932, **51**, 195r); see also E. R. Bolton, *ibid.* 1927, **46**, 44r, and "Oils, Fats, and Fatty Foods," 1928, pp. 302-316.

R. Thomas (J.S.C.I. 1920, **39**, 10r), studying different aspects of the mechanism of the hydrogenation of unsaturated glycerides in the presence of a nickel catalyst, found that the

influence of foreign gases on the catalyst and on the velocity of hydrogenation might be either purely physical or chemical. He confirmed the observation of Armstrong and Hilditch that linolein absorbs hydrogen much more rapidly than does olein. Kaufmann's thiocyanogen method of determining the degree of unsaturation of fats has also afforded proof of the selective character of hydrogenation (Kaufmann and Hansen-Schmidt, Ber. 1927, **60** [B], 50). In experiments with a nickel catalyst at 200° in an autoclave the linoleic acid in a fat had disappeared after 135 minutes.

The effects of the temperature of hydrogenation on the selective action and upon the melting-point and iodine value of the product have been studied by K. A. Williams (J.S.C.I. 1927, **46**, 446r, 448r) over a range of 120-200°.

The formation of isooleic acid is dealt with by Moore (*ibid.* 1919, **38**, 320r); Hilditch and Moore (*ibid.* 1923, **42**, 15r); Richardson, Knuth and Milligan (Ind. Eng. Chem. 1924, **16**, 519; 1925, **17**, 80) Cocks, Christian and Harding (Analyst, 1932, **56**, 368); Lush (J.S.C.I. 1923, **42**, 219r; 1924, **43**, 53r; 1925, **44**, 129r); Hilditch and Vidyarthi (Proc. Roy. Soc. 1920, A, **122**, 552).

Elaidic acid is the predominating isomer formed but a number of others also appear. The total proportion of isomers formed depends on temperature, possibly on pressure, certainly on the degree of activity of the catalyst, the relative degree of mixing of oil and catalyst, the rapidity of desorption of reacting molecules from the catalyst and the nature of the catalyst. It is most marked with platinum, less with palladium, still less with nickel and least with copper. It is promoted by high temperatures and is least marked in the continuous process. Under constant conditions, the ratio of solid isooleic acid to liquid oleic acid in the product tends to a constant value after the reaction has proceeded to a fixed extent, this value being maintained until saturation is complete. Unpublished researches of K. A. Williams suggest that the proportions and the reactions themselves are controlled by excess electronic energy acquired by hydrogen in its sorption by the catalytic metal and subsequent transfer to the oil molecule.

The theory of the catalytic action is dealt with by Rideal and Taylor, "Catalysis in Theory and Practice," 1926; Falk, "Catalytic Action," 1922; Sabatier, "Le Catalyse en Chimie Organique," 1920; various reports of the American Committee on Contact Catalysis, 1922-26; Nyrop, "Treatise on the Catalytic Action of Surfaces," Copenhagen, 1934; Hilditch, "Catalytic Processes in Applied Chemistry," 1929; H. S. Taylor (Proc. Roy. Soc. 1925, A, **108**, 105; J. Phys. Chem. 1926, **30**, 150); Bloemen (Fettechem. Umschau, 1934, **41**, 95, 151); Berkman, Morrell and Egloff, "Catalysis" Reinhold Publishing Co., New York, 1940, Hydrogenation, pp. 809-887.

Arachidic acid may still be detected in hardened arachis oil, but a modification of the usual test is necessary (see Kreis and Roth, Z. Unters. Nahr.-u. Genussm. 1913, **25**, 81).



Leimdörfer (Chem. Zentr. 1914, I, 304) has shown that the stearic acid formed in the hydrogenation of oils is chemically identical with natural stearic acid.

Marine animal oils yield a much smaller proportion of insoluble bromides after hydrogenation, and the distinctive colour reactions of the original oils are either modified or no longer obtained.

Bellier's reagent (nitric acid, sp.gr. 1.4, and resorcinol in benzene) also gives different colour reactions with hardened sesamé, cotton-seed and arachis oils from those given by the original oils. The Baudouin test for sesamé oil is intensified by hydrogenation, but Halphen's test for cotton-seed oil is inhibited, the chromogenic substance giving the reaction being destroyed after hydrogenation for 15 minutes with a nickel catalyst at 150–160°.

The amount of phytosterol is not materially reduced by hydrogenation at 200°, but cholesterol is resinified at 200°, and after treatment at 250° will no longer yield a crystalline derivative (Marcusson and Meyerheim, Z. angew. Chem. 1914, 27, 201).

Analytical data for hydrogenated oils are given by Bomer and Leschly-Hansen (J.S.C.I. 1912, 31, 996); E. Mellana (*ibid.* 1914, 33, 701); Sudborough, Watson and Athawale (*ibid.* 1923, 42, 103A); Myddleton and Barry, "Fats Natural and Synthetic," E. Benn, Ltd., 1924; Williams and Bolton (Analyst, 1924, 49, 460); Williams (J.S.C.I. 1927, 46, 446, 448r), and in other communications already referred to.

The hydrogenation of tung oil is referred to by H. I. Waterman and C. van Vlodorp (Chem. Weekblad. 1934, 31, 420) who point out that the course of the reaction varies with temperature and pressure and with the nature of the catalyst. T. Moore (Biochem. J. 1939, 33, 1635) has found that the strong spectrographic absorption at 270 $\mu$  drops, while the originally small value at 230 $\mu$  first rises and then drops, both reaching negligible values at saturation. He compares the formation of an acid with absorption maximum at 230 $\mu$ , indicated by this observation, with the formation of the same acid by hens and rats fed on tung oil. He also notes that the hydrogen absorption and drop in iodine value do not correspond in the hydrogenation of tung oil, ascribing this discrepancy to the effect of conjugated bonds.

For a study of the alteration in glyceride structure produced during the progressive hydrogenation of olive and cotton-seed oils, see Williams and Bolton (Analyst, 1924, 49, 460) and Hilditch and Jones (J.C.S. 1932, 805); and for investigations of the course of hydrogenation in the continuous process of Technical Research Works, Ltd., see Lush (J.S.C.I. 1923, 42, 219r; 1924, 43, 53r); Hilditch and Rhead (J.S.C.I. 1932, 51, 198r). Williams and Bolton (Analyst, 1924, 49, 460) base a method for detecting hydrogenated oils on the determination of isooleic acid, using the insolubility of the lead salt of the latter in ether and alcohol as a means of separating it in admixture with saturated acids from the liquid acids. This test affords a much more trustworthy indication than the presence of nickel, which is now practically eliminated from

the products of hydrogenation. J. Grossfeld and J. Peter (Z. Unters. Lebensm. 1934, 68, 345) have extended the applicability of this test.

#### NICKEL IN HYDROGENATED FATS.

The presence of a trace of the metallic catalyst was at one time of frequent occurrence in hydrogenated fats, especially those of continental origin. Bömer (Chem. Rev. Fett.-u. Marz-Ind. 1912, 19, 221) found 0.01% of ash with 0.006% of nickel oxide in hydrogenated sesamé oil, and 0.006% of ash with 0.0045% of nickel oxide in hardened whale oil. Hence, the detection of nickel in a fat indicates the presence of a hardened oil, although a negative result in the test does not necessarily prove that such products are absent, since means, such as treatment with dilute hydrochloric acid, are often employed to remove the residual metal. In experiments to ascertain the effect of traces of nickel upon the human system, Offerdahl (Ber. deut. pharm. Ges. 1913, 23, 558) found that 0.5 g. of nickel could be taken daily without any injurious effect, 99.8% of the metal being rapidly excreted from the system.

Modern edible hydrogenated fats do not usually contain more than 1 part of nickel per 10 million and often much less.

For the detection of traces of nickel the dimethylglyoxime test may be used (*see* Knapp, Analyst, 1913, 38, 102), but certain untreated oils, free from nickel, may show a similar coloration if the test is made directly on the oil. The test should therefore be applied to the ash of 100 g. of the oil for better results (Prall, Z. angew. Chem. 1915, 28, i, 40). A still more sensitive reagent for nickel is a  $\alpha$ -benzildioxime, as suggested by Atack (Analyst, 1913, 38, 316).

To obtain products relatively free from nickel, Ellis (J.S.C.I. 1912, 31, 1165) lays stress upon the importance of using the catalyst in metallic form rather than in the form of oxide, since metallic nickel will not readily combine with free fatty acids to form a soap in the presence of free hydrogen. Too rapid hydrogenation should also be avoided, so as to prevent decomposition of the fat, with liberation of water, which might cause hydrolysis of the fat and liberation of free fatty acids.

For the mechanism of the addition of hydrogen to unsaturated glycerides in the presence of nickel, *see* Thomas (J.S.C.I. 1920, 39, 107r); and for a study of the relation between the occlusive power of palladium for hydrogen and its activity in catalytic hydrogenation, *see* Maxted (J.C.S. 1921, 119, 1281).

#### NUTRITIVE VALUE OF HARDENED OILS.

The digestibility of hydrogenated fats is dealt with by Langworthy (Ind. Eng. Chem. 1923, 15, 276) who describes researches of the U.S. Department of Agriculture. The conclusion is drawn that soft hydrogenated fats are as well assimilated as natural fats, but if the melting-point is raised beyond 40–45° the digestibility falls rapidly.

The food value of hydrogenated fats is much the same as that of natural fats, but commercial hardening processes almost always destroy any

vitamins in the raw material. Diets containing a considerable proportion of hydrogenated fats are widespread and lead to no harmful effects provided that other sources of necessary vitamins are included.

K. A. W. and C. A. M.

**HARGREAVES-BIRD CELL** (Vol. III, 53b).

**HARMALA, ALKALOIDS OF PEG-ANUM HARMALA.** *Harmaline, Harmine, Harmalol, Harman, Norharman.* The seeds of the wild rue, *Peganum harmala* Linn. (Fam. Rutaceae) or harmal seeds have been employed from the earliest times in Eastern medicine as a stimulant, antelmintic, or even narcotic. They are said to be the source of a red dye produced in Southern Russia and they have been used in the manufacture of oil. Wild rue is an odoriferous herbaceous plant, 1-3 ft. high, and inhabits Southern Europe, Asia Minor, Egypt, North-western India and Southern Siberia (Flückiger, Pharm. J. 1872, [iii], 2, 229).

The seeds and root of the plant contain four alkaloids, *harmaline*,  $C_{13}H_{14}ON_2$ , first isolated by Goebel (Annalen, 1841, **38**, 363; **39**, 289), *harmine*,  $C_{13}H_{12}ON_2$ , obtained by Fritzsche (*ibid.* 1847, **64**, 360), *harmalol*,  $C_{12}H_{12}ON_2$ , first prepared by Fischer (Ber. 1885, **18**, 402) and *vasicine* (also called *peganone*), belonging to a quite different chemical type of alkaloid.

From the South American plant "yage," "caapi," "aya-huasca" or "pildé," used for the preparation of a native intoxicant (Perrot, Bull. Sci. pharmacol. 1923, **30**, 107) and which has been identified as *Banisteria caapi* (Fam. Malpighiaceae) an alkaloid has been isolated by various workers and named "telepathine," "yagine," or "banisterine" (literature: see Rouhier, *ibid.* 1926, **33**, 252; Raymond-Hamet, Compt. rend. 1927, **184**, 1266). All three alkaloids are identical with harmine; for yagine, telepathine, see Elger, Helv. Chim. Acta, 1928, **11**, 162, and Wolfes and Rumpf, Arch. Pharm. 1928, **266**, 188; for banisterine, see Brückl, Amer. Chem. Abstr. 1930, **24**, 4080 and Lewin, Chem.-Ztg. 1928, **52**, 357.

Harmal seeds contain about 4% of alkaloids, of which half to two-thirds is harmaline. The alkaloids are found for the most part in the outer portions of the seeds.

**Extraction.**—Fritzsche (*l.c.*) extracts the seeds with  $H_2O$  containing acetic or sulphuric acid. The extracts are concentrated to one-third and the phenolic harmalol separated from the other bases by precipitating the latter with a small excess of caustic potash. Harmaline and harmine are re-dissolved in acid and precipitated as hydrochlorides by a saturated solution of common salt. Harmaline and harmine are separated either by fractional precipitation with ammonia from their hydrochlorides or by fractional crystallisation from  $MeOH-C_6H_6$  (3:1 vol.). These fractionations are not accurate (*cf.* Hasenfratz, Ann. Chim. 1927, [x], **7**, 151); for an interesting separation of the two alkaloids by buffer solutions, see Elgazin, A. 1933, 408.

**Harmaline**, (I)  $C_{13}H_{14}ON_2$ , optically inactive, m.p. 230-240° (decomp.), from  $MeOH$  prisms or small tables, from  $EtOH$  rhombic octahedra, is very slightly soluble in cold

$H_2O$  or  $Et_2O$ , moderately soluble in cold and readily soluble in hot  $EtOH$ . For ultra-violet-absorption curves, see Kharash (Amer. Chem. Abstr. 1936, **30**, 2706); dissociation constants, see Orlow (Chem. Zentr. 1932, II, 70); microchemical identification, see Amelink (Pharm. Weekblad, 1931, **68**, 221).

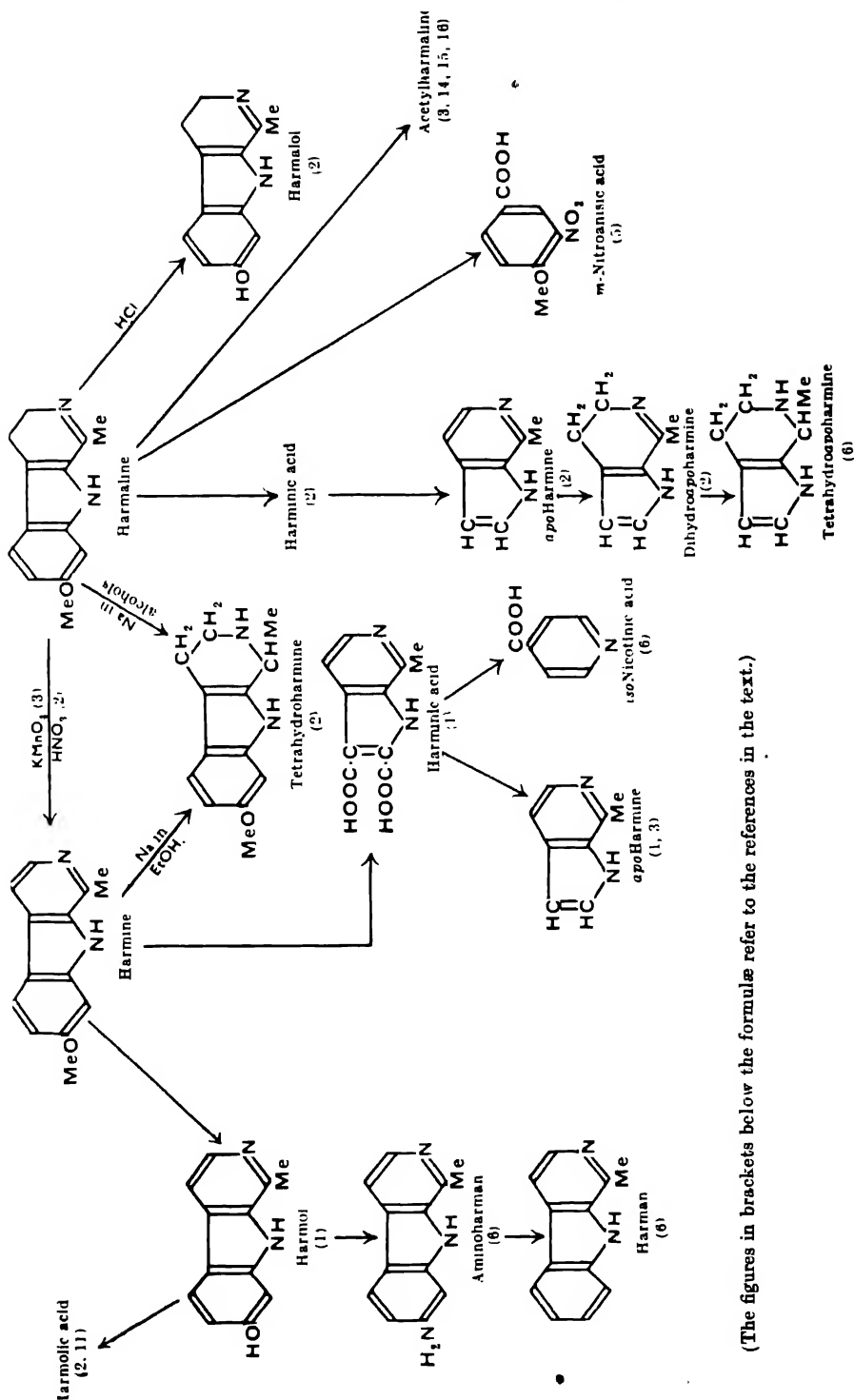
The salts are yellow:  $B \cdot HCl \cdot 2H_2O$ , slender needles; the platinichloride is microcrystalline; typical salts are the mercurichloride and the acid chromate, insoluble in  $H_2O$ . The hydrocyanide,  $B \cdot HCN$ , is still a base and combines with acids to form crystalline salts. *Acetyl derivative*, colourless needles, m.p. 204-205°, easily affected by acids. By treating (I) with  $CH_3I$ , *N-methylharmaline hydriodide* and *dimethylharmaline hydriodide* are obtained (Fischer, Ber. 1914, **47**, 102). *N-methylharmaline*, m.p. 162°, easily soluble in  $EtOH$ ,  $CHCl_3$ ,  $MeOH$ , sparingly soluble in  $Et_2O$  or  $C_6H_6$ . *N-methylharmaline* and *acetylharmaline* are derivatives of a tautomeric form of (I) (Perkin, Robinson *et al.*, J.C.S. 1924, **125**, 657).

Harmaline heated in a sealed tube with  $HCl$  yields *harmalol*,  $C_{12}H_{12}ON_2 \cdot 3H_2O$ ; by gentle oxidation with  $HNO_3$  or  $KMnO_4$  (Fischer, Ber. 1889, **22**, 640; Elgazin, A. 1934, 1117) harmine is obtained; sodium reduction in alcohol yields *dihydroharmaline* (*tetrahydroharmine*).

**Harmine**, (II)  $C_{13}H_{12}ON_2$ , optically inactive, m.p. 260-261.5°, colourless prismatic needles from  $MeOH$ , easily subliming, is insoluble in  $H_2O$  and sparingly soluble in  $EtOH$  and  $Et_2O$ . For ultra-violet absorption, dissociation constants and microchemical identification, see relevant references under (I); for crystallography, see Brückl (*l.c.*). *Harmine hydrochloride*, *platinichloride*, *oxalate* and *acid chromate* crystallise well. The salts are colourless but show a deep blue fluorescence in dilute solution (Ismailov *et al.*, Chem. Zentr. 1938, II, 3276). *Methylharmine* has m.p. 209°. On treatment with conc.  $HCl$  like (I) (see above), (II) yields *harmol*,  $C_{12}H_{10}ON_2$ , m.p. 321°, not occurring in nature.

**Harmalol**, (III)  $C_{12}H_{12}ON_2 \cdot 3H_2O$ , m.p. 212° (anhydrous) may be either extracted from the natural material or prepared from (I) by demethylation. Red needles, sparingly soluble in  $H_2O$ , soluble in  $CHCl_3$  and acetone. For preparation, see Fischer (Ber. 1889, **22**, 638). The alkyl ethers of harmalol and harmol are of some importance in chemotherapy; for their preparations, see *e.g.* Coulthard, Levene and Pyman (Biochem. J. 1933, **27**, 727; B.P. 359180, 382124; G.P. 568675).

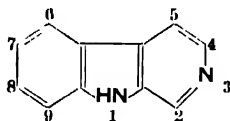
**Constitution of (I) and (II).**—(I) is dihydro-(II); both bases on reduction yield the same tetrahydro-(II); for catalytic re-oxidation, see *e.g.* Akabori and Saito (Chem. Zentr. 1930, II, 3257). Research on the constitution of the harmala bases was initiated by Fritzsche (Annalen, 1848, **64**, 360; **68**, 351; 1849, **72**, 306; 1853, **88**, 327; 1854, **92**, 330) and by O. Fischer (Ber. 1885, **18**, 400<sup>1</sup>; 1889, **22**, 637<sup>2</sup>; 1897, **30**, 2481<sup>3</sup>; 1905, **38**, 329<sup>4</sup>; 1912, **45**, 1930<sup>5</sup>; 1914, **47**, 99<sup>6</sup>) and finally concluded by the more recent researches of Perkin, Robinson *et al.* (Part I: J.C.S. 1912, **101**, 1775<sup>7</sup>; II:



(The figures in brackets below the formulæ refer to the references in the text.)

1913, 103, 1973<sup>8</sup>; III: 1919, 115, 933<sup>9</sup>; IV: 1919, 115, 967<sup>10</sup>; V: 1921, 119, 1601<sup>11</sup>; VI: 1922, 121, 1872<sup>12</sup>; VII: 1924, 125, 626<sup>13</sup>; VIII: 1924, 125, 657<sup>14</sup>; IX: 1927, 1<sup>15</sup>; X: 1929, 2942<sup>16</sup>). The arrangement of the three rings, of which two are heterocyclic, created unusual difficulties (*cf.* Perkin, Robinson *et al.*, Parts I and II); the scheme on p. 187 (in which the formulæ are written in the correct way) covers the work of Fischer and the earlier contributors.

Perkin, Robinson *et al.* (*see above* Parts III and IV) identified *harman* with a product which Hopkins (J. Physiol. 1903, 29, 451) had obtained synthetically by oxidation of tryptophan with ferric chloride (Perkin, Robinson *et al.*, Part V, p. 1616). These findings settled the arrangement of the three rings in the harmala bases and demonstrated that they are all derivatives of 3-(or  $\beta$ )-carboline or *Norharman* (4-carboline of the earlier literature): *cf.* Perkin, Robinson *et al.*, Part IV; for changes of nomenclature, *see* J.C.S. 1929, 2926, footnote.



Harman has not been found in any of the plants yielding harmine or harmaline, but Späth has found that the two bases *Aribine* (from *Arariba rubra*, Fam. Rubiaceæ) and *Loturine* (from *Symplocos racemosa*, Fam. Symplocaceæ) are identical with harman (Monatsh. 1919, 40, 351; 1920, 41, 401). Being of the nature of a proto-alkaloid, it is easily understandable that harman occurs in different families. Harman and norharman proved also to be the keystone in the elucidation of the structure of *Yohimbine*. *See* EVODIA RUTECARPA, ALKALOIDS OF.

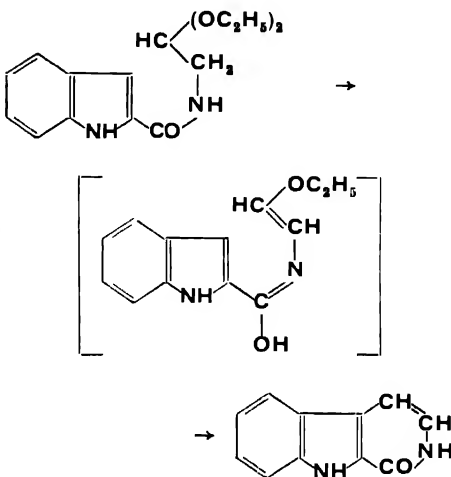
Harman,  $C_{13}H_{10}N_2$ , m.p. 238°, prisms from benzene; the sulphate, radiating clusters of short needles; the mercurichloride crystallises from dilute HCl in long slender needles. For other salts, *see* Späth (*l.c.* 1919); the ordinary salts show an intense bluish-violet fluorescence.

Norharman,  $C_{11}H_8N_2$ , crystallises from hot benzene in colourless slender needles and melts at 198.5°, sparingly soluble in cold  $C_6H_6$  or light petroleum, moderately soluble in  $Et_2O$  or ethyl acetate, readily soluble in MeOH and EtOH, also fairly soluble in hot water. A dilute acid solution exhibits a vivid fluorescence. For synthesis of norharman, *see* Perkin, Robinson *et al.*, Part V, p. 1638. The attribution of the correct position of the methoxy-group in (I) and (II) as well as the position of the double-bond in (I), is also due to these authors (*see* Parts VI and IX).

Several syntheses of the harmala alkaloids or of their derivatives have been described, they are essentially of 5 different types:

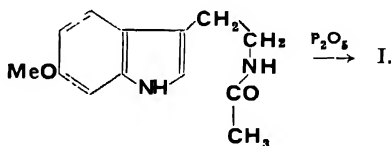
(a) Condensation of tryptophan with aldehydes and oxidation with chromic acid to harman (Perkin, Robinson *et al.*, Part V) and of 6-methoxytryptophan to harmine (Harvey and Robson, J.C.S. 1938, 97; *cf.* also Jacobs and Craig, J. Biol. Chem. 1936, 118, 760).

(b) Formation of an *isocarbostryl* by ring-closure of an indole-2-carboxy-acetalamide followed by vigorous reduction:



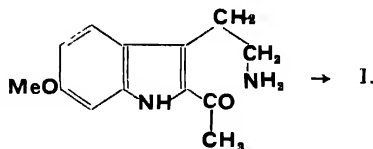
similar to the Pomeranz-Fritsch synthesis (*cf.* Fritsch, Ber. 1893, 26, 421). Synthesis of norharman, Perkin, Robinson *et al.*, Part V; condensing agent alcoholic HCl at 40°, *idem.* Part VI. Synthesis of N-methyltetrahydronorharman, *idem.* Part VI, with the same condensing agent.

(c) Formation of a dihydroharman derivative, similar to the Bischler-Napieralski synthesis of isoquinolines:



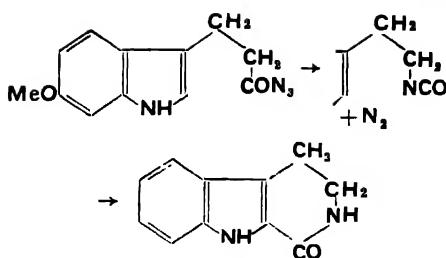
Syntheses of harmalan, harman, harmaline and harmine, *see* Späth and Lederer, Ber. 1930, 63 [B], 124, or Akabori and Saito, *ibid.* 2245; also Späth and Lederer, *ibid.* 2102; Asahina and Osada, Chem. Zentr. 1927, I, 1479; Tatsu, *ibid.* 1928, II, 668.

(d) Formation of a dihydroharman derivative by ring-closure of a  $\delta$ -aminoketone, viz.



(Perkin, Robinson *et al.*, Part IX).

(e) Formation of a ketotetrahydrocarboline by decomposition of the azide of indole-propionic acid:



(Manske and Robinson, J.C.S. 1927, 240; and Perkin, Robinson *et al.*, Part X).

For formation of harmar derivatives under "physiological" conditions, see Hahn *et al.*, Ber. 1934, **67** [B], 2031; Annalen 1935, **520**, 107, 123; Ber. 1938, **71** [B], 2163, 2175. For interesting but unsuccessful attempts at the synthesis of harmar derivatives, see also Spath and Burger, Monatsh. 1928, **49**, 265; for the synthesis of apoharmine, see Perkin, Robinson *et al.*, Part VIII.

For the pharmacology of the harmala bases, see Henry, "Plant Alkaloids," 3rd ed., 1939, p. 458 ff. where the literature is cited.

Schl.

#### HARMALINE, HARMALOL v. HARMALA ALKALOIDS.

**HARMAN** c. HARMALA ALKALOIDS and Vol. I, 466b.

**HARMINE** v. HARMALA ALKALOIDS.

**HARMOTOME** (Vol. I, 631b).

**HASHAB** (Vol. I, 11d).

**HASHISH** (Vol. II, 269c).

**HATCHETTOLITE** (Vol. I, 685c).

**HATCHETT'S BROWN** (Vol. III, 471a).

**HAUSMANNITE**. A manganese oxide, Mn<sub>3</sub>O<sub>4</sub>, crystallised in the tetragonal system, and the richest ore of manganese (Mn 72%). It forms pyramidal crystals with a good basal cleavage, and with very much the aspect of regular octahedra. They are opaque with a sub-metallic lustre and a dark brownish-black or black colour, the streak is chestnut-brown. Sp.gr. 4.7-4.8; hardness 5-5½. Well-developed crystals are found at Ilmenau in Thuringia, Bfied in the Harz, Långban in Sweden, Bigrugg in Cumberland and Miguel Burnier in Brazil. The massive black ores of manganese consist of mixtures of various manganese oxides, and doubtless hausmannite is often present, though not readily recognisable in the massive condition.

L. J. S.

**HAWKITE** (Vol. IV, 556d).

**HAWK'S EYE** (Vol. III, 430a).

**HAWTHORN** (*C. rutegus* spp.). The fruit or "haws" of the species are sometimes utilised in making sweetmeats and preserves. Otto and Kooper (Z. Unters. Nahr.- u. Genussm. 1910, **19**, 328) give the following composition of the haws of *C. coccinea*: water, 72.74; acids (as malic), 0.18; invert sugar, 7.84; sucrose, 0.12%.

A. G. Po.

**HAWTHORN PERFUME**. The natural perfume of the hawthorn, or May blossom, characteristic of *Crataegus oxyacantha*, one of the Rosaceae, is not an article of commerce. All hawthorn perfumes are mixtures of synthetic

perfumes, which may, in the most expensive types, be modified by a little of the natural perfume of some other flower which blends with the hawthorn odour. The dominant note in hawthorn perfume is struck by anisaldehyde (*q.v.*) without which no hawthorn perfume is possible. Acetophenone is the second most important constituent. Anisaldehyde is a liquid, but for "convenience," or probably greater profit, certain German manufacturers offer crystal aubepine, a compound of the aldehyde, which is only half as strong as the true aldehyde, and far less economical.

Numerous modifiers and fixatives are used, and the following may serve as a basic formula which can be modified as required.

	Patts.
Anisaldehyde . . . . .	100
Acetophenone . . . . .	5-8
Coumarin . . . . .	2-5
Dimethyl-hydroquinone . . . . .	1-3
Heliotropin . . . . .	5
Vanillin . . . . .	0.5
Linalol . . . . .	5
Geraniol . . . . .	5
Phenylacetaldehyde . . . . .	1-2

Traces of benzaldehyde and amyl salicylate are useful, and synthetic neroli oil in small quantity is an effective modifier. Artificial musk is rather too pronounced to be used as a fixative, but a small quantity of cinnamic alcohol or tincture of benzoin may be employed for this purpose.

E. J. P.

**HAZELNUT OIL**. The seed-kernels of the European hazel (filbert) *Corylus avellana* L. contain about 50-65% of oil, of which the bulk can be recovered by expression as a golden- or lemon-yellow oil having the characteristic odour of hazelnuts, which assists in its identification in admixture with other oils. The oil is used in perfumery and pharmacy and is prized in Switzerland as an edible (salad) oil. It has also been used as a lubricant for fine machinery, and, on occasion, to adulterate almond oil, or as a substitute for peach kernel oil (*cf.* Bennett, Chemist and Druggist, 1908, **72**, 89). The possible presence of hazelnut oil in the extracted fat must be taken into consideration in the analysis of chocolate containing nut-fragments (*cf.* Fincke, "Handbuch der Kakao-Erzeugnisse," Berlin, 1936).

The following values for genuine samples of hazelnut oil are drawn from recent observations (*cf.* Pritzker and Jungkunz, Z. Unters. Nahr.- u. Genussm. 1921, **42**, 232; Schuette and Chang, J. Amer. Chem. Soc. 1933, **55**, 3333; Bertram, Öle, Fette Wachse, 1936, No. 14, p. 2):  $d_{4}^{20}$  0.9152-0.9156,  $d_{20}^{20}$  0.9144,  $n_D^{20}$  1.4691-1.4698; acid value 0.3-1.7; saponification value 189-192; iodine value 84.7-86.8; thiocyanogen value 82.1 (S. and C.); Reichert-Meissl value 1.5 (P. and J.), 2.7-3.0 (S. and C.); Polenske value 0.5-0.7; unsaponifiable matter 0.35-0.58%. The composition of the fatty acids of an oil expressed from fresh nuts of Italian origin was determined by Schuette and Chang as follows: (calculated to per cent. fatty acids on oil) myristic

acid 0.2, palmitic acid 3.1, stearic acid 1.0, oleic acid 88.1 and linolic acid 2.9. (The residual oil in the nuts, subsequently extracted by light petroleum, contained a slightly higher proportion of linoleic acid (4.6%) and palmitic acid (3.6%).) Bertram records somewhat different proportions for an oil extracted by light petroleum from French nuts, viz. saturated acids 8%, oleic acid 78.2% and linoleic acid 9.1%. Arachidic acid is absent; hence the isolation of this acid serves as a means of detecting adulteration with arachis oil (Pritzker and Jungkunz, *l.c.*). Adulteration of hazelnut oil with olive oil may be detected by the high freezing-point of the sample, for the pure oil has a solidification point of  $-17$  to  $-20^{\circ}\text{C}$ . (cf. Fabris and Settimi, *Atti VI Cong. intern. Chim. appl. (Rome)*, 1907, 5, 755; Girard, *Monit. Sci.* 1889, 3, 1181). Owing to the low content of linoleic acid, the separation of the saturated acids by the Twitchell method is attended with considerable difficulty (Bertram, *l.c.*).

E. L.

**HEATHER or CALLUNA VULGARIS.**

In former times the common heath or heather, then named *Erica vulgaris*, was used as a dye-stuff for producing a yellow colour on woollen goods (Crookes, "Dyeing and Calico Printing," 1874, p. 511). All the five species of *Erica* or heather found in Great Britain were believed by Bancroft ("Philosophy of Permanent Colours," 1813, II, 108) to be capable of giving yellows much like those obtained from dyer's broom. The experiments of Hummel, however, showed that *E. tetralix* (bell heather) and *E. cinerea* contain only traces of yellow colouring matter. Heather possesses tanning property and, according to H. R. Proctor, contains 6.4% of tannin. The colouring matter, *quercetin*, was isolated by Perkin and Newbury (*J.C.S.* 1899, 75, 837) from an aqueous extract of the green portion of the plant, in which only it appears to exist.

The dyeing properties of heather are similar to those of quercitron bark; it is necessary, however, to employ 36 parts of the heather to obtain the effect given by 10 parts of quercitron bark.

A. G. P. and E. J. C.

**HEAVY ALLOY.** The "G.E.C. Heavy Alloy" which is 50% heavier than lead, has a tensile strength about equal to that of steel, with excellent machining properties. Its percentage composition is: 90 tungsten, 7.5 nickel, 2.5 copper (*Nature*, 1941, 148, 507).

**HEDENBERGITE** (Vol. III, 573a).

**HEDGE-MUSTARD SEED OIL** (Wild Radish-, White Charlock-Seed Oil) occurs to the extent of 20–35% in the seeds of the common European field weed *Raphanus raphanistrum* L., which belongs to the same Family, *Crucifera*, as the rape and ravison plants. Hedge-mustard seed was collected, and the oil was expressed on a large scale for the first time in Hungary in 1880 on the occasion of the failure of the rape-seed harvest. The crude expressed oil has a dark olive-green colour; in odour, taste and chemical and physical properties it closely resembles rape oil, and frequently appears on the market in admixture with this oil, or even under its name. The

following figures indicate the analytical characteristics which have been recorded by various investigators:  $d_{4}^{20}$  0.9175–0.9186;  $n_D^{20}$  1.4722, f.p.  $-13$  to  $-14^{\circ}\text{C}$ .; acid value 2–16; saponification value 174–179; iodine value 105–109 (*N.B.*, this value lies on, or just above, the upper limit of the iodine value of rape oils); Reichert-Meissl value 0.7–1.4; Polenske value 0.7–0.95. (Cf. Valenta, *Dinglers Polytech. J.* 1883, 277, 36; Grimme, *Chem. Rev.* 1912, 19, 104; Klumont, *Z. angew. Chem.* 1911, 24, 254; Knorr, *Seifens.-Ztg.* 1917, 44, 234; Bureš, *Chim. et. Ind.* 1933, Spec. No. (12<sup>e</sup> Congrès de Chim. ind., Prague (1932), 1073)).

According to Bureš, the fatty acids from the oil include arachidic acid (*ca.* 1.5%), linolenic acid (*ca.* 6%), linoleic acid (*ca.* 9%) with large amounts of "rapic acid" and small amounts of oleic and erucic acids. The content of erucic acid (1.5%) suggested by Bureš appears to be too low, in view of the saponification value of the oil and of the composition of oils from allied members of the same plant family. The identification of the "rapic acid" (which was based upon its low freezing-point as compared with pure oleic acid) requires confirmation, since it has been shown (Hilditch, Riley and Vidyarthi, *J.S.C.I.* 1927, 46, 462r) that the so-called "rapic acid" formerly reported to be characteristic of rape oil actually consists of ordinary oleic acid with, at most, very small amounts (*ca.* 1%) of its isomerides. Bureš and Sedlár report the isolation of a phytosterol, *raphansterol*, m.p.  $136^{\circ}$ ,  $\text{C}_{27}\text{H}_{54}\text{OH}$ , from the unsaponifiable matter of hedge-mustard seed oil (*Almanah Kong. Slov. Apot.* 3rd Congr., Belgrade-Zagreb-Spalato, 1934, 221 (1935); *Amer. Chem. Abstr.* 1937, 108).

Owing to the similarity of the two oils, the detection of hedge-mustard seed oil in rape-seed oil is extremely difficult. According to Valenta, the most characteristic test (applicable when fairly large quantities of hedge-mustard seed oil are present) is the appearance of a green coloration when the oil is partially saponified with alcoholic potash, and the concentrated filtered soap solution is decomposed with excess of hydrochloric acid.

E. L.

"**HEDONAL.**" *sec*-Amyl carbamate,



m.p.  $74^{\circ}$ , b.p.  $215^{\circ}$  (G.P. 120865). Has been used to a small extent as a hypnotic.

**HEDYOTINE.** Hedyotine was isolated by Dey and Lakshminarayana from *Hedyotis auricularia* (Fam. Rubiaceae) (*Arch. Pharm.* 1933, 271, 485). This plant grows wild in the wet lands of the Western Ghats, throughout the length of the Indian Peninsula from the Konkan to Cape Comorin, extending to Ceylon. The inhabitants of South Kanara use it specially for intestinal troubles and dysentery. For further details, see Chopra, "Indigenous Drugs of India," Calcutta, 1933, p. 323.

Hedyotine,  $\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}_3$ , is a yellow amorphous, very unstable base, decomposing rapidly when dried in a desiccator. Only the salts were obtained in pure form, they crystallise easily and are but slightly soluble in  $\text{H}_2\text{O}$ .

$C_{10}H_{22}O_3N_2 \cdot HCl$ , m.p.  $245^\circ$  (sintering at  $227^\circ$ ), dissolves in 400 parts of  $H_2O$  at room temperature, is easily soluble in  $MeOH$  and  $EtOH$ ; *nitrate*, m.p.  $252^\circ$  (sintering at  $238^\circ$ ); *picrate*, m.p.  $265^\circ$ .

The chemical structure of hedyotine has not yet been elucidated.

Schl.

"**HEGONON.**" A preparation from albumose and ammoniacal silver salts in which the metal appears mainly in the colloidal condition (Gjaldbæk, Dansk Tidsskr. Farm. 1929, 3, 133). It is of value for its antigonococcal action (Pharm. Zentr. 1931, 72, 362; Mandl, Wien. klin. Woch. 1932, 45, 918).

**HELENIN.** The lipochrome of *Helenium autumnale* is helenien,  $C_{72}H_{116}O_4$ . It separates in dark red needles from ethyl alcohol, m.p.  $92^\circ$ , and exhibits absorption maxima at 5110, 4780 and 4660 Å. (in carbon disulphide). It is the dipalmitate of lutein. Helenien also occurs in *Cheiranthus*, *Arnica montana*, *Helopsis*, etc. (Kuhn and Winterstein, Naturwiss. 1930, 18, 418, 754; Kuhn, Winterstein and Lederer, Z. physiol. Chem. 1931, 197, 150; Winterstein, Angew. Chem. 1934, 47, 315)

F. S. S.

**HELENIN** (v. Vol. I, 175b).

**HELIANTHIC ACID.** An acid isolated from sunflower seeds (Ludwig and Kromayer, Arch. Pharm. 1859, [1], 99, 11) and later identified with chlorogenic acid,  $C_{16}H_{18}O_9$  (q.v.) (Gorter, Arch. Pharm. 1909, 247, 436).

"**HELICON**" (v. Vol. I, 517d).

**HELINDONE COLOURS** (v. Vol. I, 232c).

**HELINUS OVATUS.** (Fam. Rhamnaceæ.) A climbing shrub indigenous to South Africa. It was examined chemically by Goodson (J.C.S. 1920, 117, 140) who isolated from the leaves acetic acid, quercitol, a saponin and scyllitol.

**HELIODOR** (v. Vol. I, 685b).

"**HELIO**" **DYESTUFFS** and **PIGMENTS** (v. Vol. IV, 236a, b).

**HELIO FAST YELLOW** (v. Vol. I, 233a).

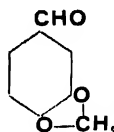
**HELIOTROPE** (v. Vol. II, 25a, 517c).

**HELIOTROPE PERFUME.** The common heliotrope, *Heliotropium europæum* (Fam. Boraginæ) is a native of the south and west of Europe, and its flowers are used for the preparation of perfumes, but owing to the discovery of synthetic heliotropin (piperonal) the natural perfume finds a very limited employment. The plant is known in this country as "cherry pie." Several members of the *Compositæ* are known as heliotrope on the Continent. Most of the artificial heliotrope perfumes contain modifiers of the geraniol type, the basic ingredients being heliotropin, with a little vanillin, coumarin and dimethylhydroquinone.

E. J. P.

**HELIOTROPIN.** This valuable synthetic perfume, also known as piperonal, is a crystalline compound having a powerful odour of heliotrope. It occurs naturally in various plants, but it does not pay to extract it, as it can be prepared artificially at a much lower cost. It was originally prepared from the base piperine, from pepper berries. This is today merely a matter

of historical interest. Heliotropin is the methylene ether of protocatechuic aldehyde of the following constitution:



It crystallises in needles, m.p.  $37^\circ$ ; forms two oximes, m.p.  $112^\circ$  and  $146^\circ$  respectively, and a semicarbazone, m.p.  $140^\circ$ .

In commerce it is prepared from safrol, which is isomerised to isosafrol by boiling with caustic alkali. Five parts of such isosafrol are oxidised by a solution of 25 parts of potassium dichromate, 38 parts of sulphuric acid and 80 parts of water. The reaction product is steam distilled, the distillate extracted with ether, and the heliotropin so obtained is purified in the usual manner.

Heliotropin should be stored in a cool dark place, as otherwise it is liable to decomposition. It is used in many perfumes, and blends well with coumarin, vanillin or with lemon, bergamot and neroli oils.

E. J. P.

**HELIUM.** Sym. He. At. no. 2. At. wt. 4.003 (cf. Baxter, Honigschmid and Lebeau, Eighth Report of Committee on atomic weights, International Union of Chemistry, Ber. 1938, 71 [A], 93. Bainbridge and Jordan (Rev. Mod. Physics, 1937, 9, 370) have obtained the value 4.00389, and Aston (Nature, 1936, 137, 357, 613) the value 4.00391; both these values were obtained by mass-spectrographic methods, and they are referred to the physical scale, in which  $^{16}O=16.00000$ . After applying the correction factor, 1.00027, for conversion to the chemical scale (naturally occurring oxygen= $16.00000$ ), the mean value becomes 4.00285, with a probable error of about 1 unit in the fourth place). Isotopes: natural helium probably contains the single atomic species  $^4He$ ; Bleakney, Harnwell, Lozier, Smith and Smyth (Phys. Rev. 1934, [ii], 46, 81) find that ordinary helium contains less than 1:10<sup>6</sup> and 1:10<sup>6</sup> of  $^3He$  and  $^6He$ , respectively.

Helium is a gaseous element which is the lightest member of the group of "rare" or "inert" gases discovered late in the last century by Rayleigh and Ramsay, and which now forms Group 0 in the Periodic Classification of the elements. Helium is the lightest gas known, with the exception of hydrogen, and its most striking property is its complete chemical inertness.

#### HISTORY.

Helium was discovered spectroscopically in the sun nearly 30 years before its presence in the earth was recognised. During the solar eclipse of August 18, 1868, a bright yellow line was observed in the spectrum of the solar chromosphere; this was generally thought to be the D doublet of sodium, but Janssen (Compt. rend. 1868, 67, 838) showed that it did not coincide with the sodium lines. On October 20 of the

same year, Lockyer observed the new line in the spectrum of a solar protuberance, but regarded it as a new hydrogen line (Proc. Roy. Soc. 1869, **17**, 91, 131, 288; Phil. Mag. 1869, [iv], **38**, 66). Later, however, Lockyer recognised that the yellow line (which was called  $D_3$  on account of its association with the sodium lines, and had a measured wave-length of 5,876 Å.) was due to a new element, which he named *helium*, from the Greek *ἥλιος*, the sun; Lockyer also attributed other unassigned lines in the solar spectrum, at 5,016, 4,922 and 6,678 Å., to helium (Proc. Roy. Soc. 1870, **18**, 354). Young (Amer. J. Sci. 1872, [ii], **4**, 356) also assigned a line at 4,472 Å. to the new element. Helium lines were soon discovered in the spectra of hot stars by Secchi (Compt. rend. 1869, **68**, 237, 359). A general account of the discovery of helium in the sun is given by Lockyer (Nature, 1896, **53**, 319).

In 1881 Palmieri (Rend. Accad. Sci. Fis. Mat. Napoli, 1881, **20**, 233; Gazzetta, 1882, **12**, 556) claimed to have observed the  $D_3$  line in the spectrum of a Bunsen flame into which certain volcanic products from Vesuvius had been introduced, but the observation is almost certainly incorrect as helium lines cannot be excited by such means. Later Hillebrand (Bull. U.S. Geol. Survey, 1891, **78**, 43; Amer. J. Sci. 1890, [iii], **40**, 384; 1892, [iii], **42**, 390) obtained an inert gas on treating certain uranium minerals with sulphuric acid, or on fusing them with sodium carbonate; the gas was not studied fully, but it was thought from its spectrum to be nitrogen, although the existence in the spectrum of unidentified lines was duly noted. Ramsay, doubting the production of gaseous nitrogen in the sulphuric acid reaction, suspected that the gas might have been argon, and undertook a more detailed examination of the gas from cleveite. He found an inert residue which would not combine with oxygen on long sparking; its spectrum was examined by Ramsay, and by Crookes, who recognised the bright yellow  $D_3$  line of helium, in addition to argon lines (cf. Proc. Roy. Soc. 1895, **58**, 65, 67, 81; Chem. News, 1895, **71**, 151). The occurrence of helium in gases from uranium minerals was discovered independently a few days later by Langlet, at Upsala (cf. Cleve, Compt. rend. 1895, **120**, 834). Further research showed that the cleveite gas consisted of much helium, with traces of argon and some hydrogen, carbon dioxide and nitrogen; the last three gases were removed by sparking with oxygen over potassium hydroxide solution. The density of helium was found to be not greater than 2.13, and the ratio of its specific heats (1.65) showed that helium resembles argon in being monatomic; the atomic weight was thus stated to be not more than 4.26 (Ramsay, Collie and Travers, J.C.S. 1895, **67**, 684). The  $D_3$  line in the spectrum of terrestrial helium was afterwards found to be a doublet (Runge, Nature, 1895, **52**, 128), and its identity with solar "helium" was doubted, but the solar  $D_3$  line was also found to be double (Lockyer and Hale, *ibid.*, p. 327; Proc. Roy. Soc. 1896, **59**, 4) and the identity of the elements was thus established. A number of workers have doubted the elementary nature of helium on account of the

complexity of its spectrum, but all attempts to separate the gas into two or more constituents have failed (see Ramsay and Travers, *ibid.* 1898, **62**, 316).

Helium was first detected in the atmosphere by Kayser (Chem. News, 1895, **72**, 89), who observed its lines in the spectrum of crude argon preparations obtained from air. The production of helium during disintegration of radioactive elements, which explains its presence in uranium minerals, was discovered by Soddy in 1903.

For an account and bibliography of the early investigations on helium, see Ramsay, Ann. Chim. 1898, [vii], **13**, 433, and Travers, "The Discovery of the Rare Gases," London, 1928.

#### OCCURRENCE.

*In the Sun, Stars and Nebulae.*—Helium has been detected spectroscopically in the chromosphere of the sun, in which it also occurs in an ionised form, and in protuberances and sunspots (cf. Pringsheim, "Vorlesungen über die Physik der Sonne," Leipzig, 1910). Helium is also present in nebulae, the planetary "mist," fixed stars, and *novæ*, or stars of recent origin. The occurrence of helium is related to the temperature of the star (Lockyer, Proc. Roy. Soc. 1897, **61**, 148). The spectra of *novæ* contain helium absorption lines displaced towards the violet, showing that the gas is in radial movement towards the observer and away from the stars (Eddington, "Expanding Universe," 1933, p. 11). Helium is present to the extent of  $0.23\text{--}36 \times 10^{-6}$  c.c. per g. in certain specimens of meteoric iron, from which it is liberated by dissolution in acid (Paneth *et al.*, Z. Elektrochem, 1928, **34**, 645, 648; Z. physikal. Chem. 1931, **152**, 127). The rôle of helium in the evolution of the universe and development of stars of various types is discussed by Saha (Phil. Mag. 1920, [vii], **40**, 472; 1921, [vi], **41**, 267, 809; Proc. Roy. Soc. 1921, A, **99**, 135; Z. Physik, 1921, **6**, 40).

*In the Earth's Atmosphere.*—Numerous workers have shown the existence of small amounts of helium in the atmosphere, of which it forms about 0.0005% by volume, or 0.00007% by weight (Claude, Compt. rend. 1909, **148**, 1454; Watson, J.C.S. 1910, **97**, 810). It has been claimed that the helium content of air should increase in the upper layers of the atmosphere; Paneth and Gluckauf (Nature, 1935, **136**, 717) have found that the helium content is constant up to an altitude of about 18 km., but is increased by 8% at 21 km. According to one theory the atmosphere should consist almost entirely of hydrogen and helium at altitudes greater than about 100 km., the content of helium falling with increasing height (Jeans, "Dynamical Theory of Gases," Cambridge, 1925). Convincing evidence in favour of such theories appears to be lacking.

*In Volcanic Gases, Hot Spring Gases, etc.*—Small percentages of helium are of frequent occurrence in gases of volcanic origin. The proportion of helium and the yield of gas vary between very wide limits in different regions, and rich helium sources are usually localised. A number of hot springs yielding gases rich in



helium are grouped round a line drawn through the French towns of Moulins, Dijon and Vesoul. Details of some of the more prolific French springs are tabulated below; the figures are taken from Moureu and Lepape, *Compt. rend.* 1912, 155, 197; *see also* Moureu, *J.C.S.* 1923, 123, 1913.

Location and name of spring.	Percentage of helium in gas.	Yield in litres per year.	
		Total gas.	Helium.
Santenay (Côte d'Or):			
Source Lithium	10.16	51,000	5,182
Source Carnot	9.97	179,000	17,845
Source Fontaine-Salée	8.40	—	—
Maizières (Côte d'Or):			
Source Romaine	5.92	18,250	1,080
Grisy (Saône-et-Loire):			
Source d'Ys	2.18	—	—
Bourbon Lancy (Saône-et-Loire):			
Source du Lymbce	1.84	547,500	10,074
Néris (Allier):			
Source César	0.97	3,504,000	33,990
La Bourboule (Puy-de-Dôme):			
Source Choussay	0.01	30,484,800	3,048

The helium content of 8–10% recorded at Santenay are very exceptional. Many other French springs liberate helium-bearing gas, but the helium contents fluctuate considerably. The neighbouring European countries also possess springs yielding helium, but the quantities are generally much smaller. The King's Well, Bath, England, gives a gas containing about 0.15% of helium, but the annual yield is small. A few German spring gases (*e.g.* from Baden-Baden and Wildbad) contain about 1% of helium (*cf.* Sieveking and Lautenschlager, *Physikal. Z.* 1912, 13, 1043). According to Von Angerer and Funk (*Z. physikal. Chem.* 1933, B, 20, 368) a spring at Dürkheim is the only German source which yields a gas comparable in helium content with American natural gas, *i.e.* containing 1–2% of helium. The famous *soffioni* of Tuscany contain some helium (*e.g.* 0.0155% of helium in gas from Larderello). Gases containing 0.002–0.0146% are obtained from natural sources in Iceland. New Zealand natural gases almost always contain some helium (Farr and Rogers, *New Zealand J. Sci. Tech.* 1929, 10, 300). Details of many other sources are given by Moureu, *J.C.S.* 1923, 123, 1905, and in Abegg's "Handbuch der anorganischen Chemie," Vol. IV, Section 3, Part 1 ("Die Edelgase").

It is generally accepted that naturally occurring helium has been produced by radioactive

disintegration, but the quantities available over small areas indicate that the supplies are being drawn from gas which has accumulated during past ages, and not from continuous radioactive sources. Prolific helium sources occur where local conditions have favoured the accumulation of the gas in underlying strata. It is estimated that the earth's crust contains radioactive material equivalent to about  $2.4 \times 10^{20}$  g. of uranium, which would produce approximately  $2 \times 10^7$  cu. m. of helium per year. If this estimate is correct considerable quantities of helium have been lost from the earth during geological time, possibly by diffusion into space. Interesting regularities in the composition of helium-bearing gases have been noted; the helium content of hot-spring gases is usually small if they contain a large proportion of carbon dioxide. Lepape (*Compt. rend.* 1935, 200, 163, 336) has observed that gases rich in helium are associated with springs yielding larger quantities of lithium salts, and that sources very rich in helium also yield rubidium and caesium salts; it is suggested that the helium has resulted from the radioactive decomposition of element 87, the alkali-metal which still remains to be isolated.

*In Deposits Associated with Hydrocarbons: Natural Gas.*—Gases from mineral springs contain a very large proportion of nitrogen, or, less frequently, carbon dioxide. The "natural gas" occurring in the United States and elsewhere is of a different type, and contains large amounts of methane, ethane and other hydrocarbons. The natural-gas sources are "dry" wells, and the deposits are usually associated with petroleum. The presence of helium in American natural gas was discovered by Cady and McFarland (*J. Amer. Chem. Soc.* 1907, 29, 1523; *see also* *Ind. Eng. Chem.* 1938, 30, 845), who found helium contents of up to 1.48% in specimens of gas from various localities. The natural gas wells in the United States now form the principal commercial source of helium. The helium-rich wells occur chiefly in the States of Kansas, Oklahoma and Texas, with less important regions in Ohio, Montana and California. Typical analyses of natural gas are given in the table on the next page; the figures are due to Moore (*J. Franklin Inst.* 1921, 191, 145; *Ind. Eng. Chem.* 1926, 18, 198) (*see also* Cady and McFarland, *l.c.*).

The amount of helium liberated from United States gas wells has been estimated at 18 million cu. m. per year (Moore, *l.c.*); the total quantity available is assessed at some thousand million cu. m. As remarked above, such large supplies can only be due to accumulation of helium under favourable geological conditions during past ages. Although the helium wells are located in oil-bearing regions, it is noteworthy that "mixed" sources of helium and oil are rare, the helium wells being completely dry. In the famous Petrolia field, which has supplied large quantities of helium for commercial undertakings, the gas originates in strata 500 metres below the surface, but oil is obtained at a depth of only 100 metres.

Natural gases containing about 0.3% of helium occur in Alberta and Ontario, Canada;

Field.	Location.	Composition of gas, %.					
		N <sub>2</sub> .	CH <sub>4</sub> .	C <sub>2</sub> H <sub>6</sub> , etc.	O <sub>2</sub> .	CO <sub>2</sub> .	He.
Rogers.	Chautauqua, Kansas.	43.69	54.20	0.00	0.83	0.00	1.28
Petroba.	Clay, Texas.	31.13	56.85	10.33	0.54	0.25	0.90
Pearson.	Osage, Oklahoma.	39.59	59.33	0.00	0.45	0.00	0.63
Augusta.	Butler, Kansas.	11.08	74.74	12.92	0.57	0.19	0.50
Big Bell.	Montgomery, Kansas.	21.49	72.23	5.10	0.69	0.08	0.41
Glen Mary.	Scott, Tennessee.	3.22	63.86	31.73	0.65	0.18	0.36
Pavilion.	Genesee, New York.	2.56	87.96	8.68	0.49	0.00	0.31
Breckenridge.	Stephens, Texas.	13.50	76.48	19.68	0.12	0.00	0.21
Beaver Creek.	Floyd, Kentucky.	0.37	77.55	21.13	0.66	0.16	0.13
Lance Creek.	Niobrara, Wyoming.	0.92	69.06	29.19	0.63	0.20	trace

the deposits are probably related geographically to those in Montana, U.S. Natural gas sources yielding helium also occur in certain parts of Europe: the most prolific is at Neuengamme, near Hamburg, where a gas containing 0.015–0.025% of helium is liberated, corresponding to 25,000 cu. m. of the latter gas per year (Czako, Z. anorg. Chem. 1913, **82**, 249). A rich source (0.095%; 20,000 cu. m. per year) is recorded at Vaux-en-Bugey, France, and a relatively high percentage of helium is given for a well at Lesquin, near Lille (0.924%; 1,359 cu. m. per year) (cf. Moureu, J.C.S. 1923, **123**, 1905). Clay (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 529) records that petroleum gases from Indian sources contain 0.0006–0.0033% of helium.

The ratio of helium to nitrogen in fire-damp is often much greater than the corresponding ratio for air, and fire-damp has been found to contain as much as 0.05% of helium. The yearly loss of helium into the atmosphere from underground workings must be considerable, as large volumes of gas are discharged.

*In Minerals and Rocks.*—Minerals which contain appreciable quantities of helium generally contain thorium or uranium, from which the helium has been produced by radioactive changes. Strutt (Proc. Roy. Soc. 1908, A, **80**, 572), using very delicate means of detection, has shown that traces of helium occur in a very wide variety of minerals. The gas occurs in solid solution or in minute cavities in the mineral, and is not chemically combined. The highest helium contents have been found in specimens of thorianite and uraninite (of which cleveite and pitchblende are particular varieties), these contain up to 0.19% (10.5 c.c. per g.) and 0.13–0.15% (7.2–8.1 c.c. per g.; cleveite), respectively (cf. Sieverts and Bergner, Ber. 1912, **45**, 2576; Dunstan and Blake, Proc. Roy. Soc. 1905, A, **76**, 253; Ramsay, Ann. Chim. 1898, [vii], **13**, 433; Abegg, *op. cit.* pp. 55–67). Monazite, a mineral available in relatively large quantities, often contains about 1 c.c. of helium per g., and has been used as a secondary commercial source of the gas. The quantity of helium obtained from a mineral of known uranium or thorium content has been used to estimate the

geological age of the mineral, as a given mass of uranium or thorium produces a fixed volume of helium per year by radioactive disintegration. The ages obtained by this method vary from 100,000 years for more recent strata to 600 million years for rocks of the lower pre-Cambrian period (Lawson, Naturwiss. 1917, **5**, 429, 452). The ages obtained by the helium method are less than those derived from determinations on lead isotopes, suggesting that partial loss of the helium has occurred.

#### PREPARATION.

*In the Laboratory.*—Helium may be obtained from the minerals named above by heating with dilute sulphuric acid, fusion with alkali, alkali hydrogen sulphate, pyrosulphate or dichromate, or by heating the mineral in a vacuum. The last-named process is the simplest, but a temperature of 1,000–1,200° is necessary if the maximum yield of helium is to be obtained; about 50% of the gas available in the mineral is evolved on heating to a red heat in a hard-glass tube (Wood, Proc. Roy. Soc. 1910, A, **84**, 70). A larger but still not quantitative yield is given by the fusion process, which is comparatively rapid: a hard-glass tube about a metre long is charged with successive layers of magnesium carbonate (10 cm.), a mixture of 3 parts by weight of finely powdered cleveite and 2 parts of potassium pyrosulphate (Travers used equal weights of the powdered mineral and potassium hydrogen sulphate), kept in position with an asbestos plug, copper oxide, powdered magnesium and phosphorus pentoxide. When the tube is heated in a suitable furnace the magnesium carbonate produces a stream of carbon dioxide, in which the helium is carried off and collected over potassium hydroxide solution (cf. Langlet, Z. anorg. Chem. 1895, **10**, 289). The fusion method often gives trouble in practice owing to frothing and breakage of the tube. The most convenient method is to decompose the mineral completely with sulphuric acid; Ewers (Ann. Phys. 1905, [iv], **17**, 797) gives the following details of the extraction process: 150 g. of finely powdered cleveite are mixed to a paste with water in a 500 c.c. flask. Air in the

flask is displaced with a current of carbon dioxide, and 225 c.c. of concentrated sulphuric acid are added through a dropping funnel. The helium evolved is removed by a slow stream of carbon dioxide, and collected over potassium hydroxide solution. Cleveite is a fairly cheap laboratory source of helium, as 1 kg. of the mineral should yield up to 8 litres of the gas. A much commoner mineral which contains workable quantities of helium is monazite, large supplies of which are used in the extraction of cerium, thorium and rare-earth metals; monazite affords up to a litre of helium per kilogram, and the gas is extracted by heating to 1,000°. The Auer-Gesellschaft have marketed crude (75%) helium obtained by this method as a by-product of gas-mantle manufacture.

Minerals liberate helium slowly in a vacuum at room temperature, and a small proportion is evolved on powdering the mineral; Gray (Proc. Roy. Soc. 1909, A, 82, 301) recovered 28% of the available helium in thorianite by powdering to a particle diameter of  $3\mu$ , but a further reduction in size gave no additional yield.

Helium may also be isolated from the rare-gas mixture obtained from atmospheric nitrogen by passing it over heated magnesium (Ramsay and Travers, *ibid.* 1899, 64, 183) or a heated mixture of magnesium and quicklime (Maquenne, Compt. rend. 1895, 121, 1147), but the process is very laborious and the yield is at most 1 litre of helium from 200,000 litres of air. The residues obtained commercially from the fractional distillation of liquid air are, however, a practical source of helium (*see below*). Mineral springs have also been made to yield small quantities of helium for laboratory use; Ramsay obtained it from King's Well, Bath (Proc. Roy. Soc. 1896, 59, 198).

The purification of the crude helium obtained by any of the above methods is conveniently effected by fractional adsorption; as the other inert gases with which helium is associated are also inert chemically, no chemical purification method is applicable. The crude gas is introduced into an evacuated tube containing adsorbent charcoal, which is cooled in liquid air; all the inert gases except helium and neon then condense, and the helium-neon mixture can be pumped off. The vapour pressure of neon is so much less than that of helium at liquid air temperatures that a systematic repetition of the process gives fairly pure helium (Ramsay, *ibid.* 1905, A, 76, 111; Watson, J.C.S. 1910, 97, 812). The adsorption process can be rendered continuous (Edwards and Elworthy, Trans. Roy. Soc. Canada, 1919, 13, III, 47). According to Peters (Z. physikal. Chem. 1937, A, 180, 44), the adsorptive separation of neon and helium on charcoal can be completed by cooling to  $-225^\circ$ . Fused quartz at 1,000–1,200° is permeable to helium, and if a heated quartz tube is surrounded with the impure gas, pure helium can be pumped from the interior of the tube. The conditions necessary for a sharp separation appear to be somewhat critical; Watson (*l.c.*) records that the process is not successful with all kinds of fused quartz. Paneth and Peters (*ibid.* 1928, B, 1, 253) have effected a complete separation of helium from neon by a similar process

of diffusion through hot glass; they also record that palladium is permeable to hydrogen but not to helium, affording a simple method of separation for these two gases.

*On the Commercial Scale.*—The principal commercial source of helium to-day is the plant set up by the United States Government at Amarillo, Texas, for the extraction of helium from natural gas. The use of helium on a commercial scale, and for airships, has only been possible since the vast resources of the American natural-gas wells have been utilised. The natural gas used at Amarillo is collected at a pressure of 700 lb. per sq. in. on the neighbouring Cliffside field; it contains about 1.75% of helium. Traces of carbon dioxide are first removed by treating the gas with sodium hydroxide solution in large towers; this process is important as carbon dioxide solidifies and chokes up the liquefaction apparatus if it is allowed to remain in the gas. The natural gas is then cooled to  $-185^\circ$  under 300 lb. pressure, when all the constituent gases liquefy except helium and some nitrogen, which are pumped away; the liquid residue is allowed to vaporise and cool the incoming natural gas, and is then sold as a by-product for heating purposes. The crude gas containing about 50% of helium is purified by a similar liquefaction process under 2,500 lb. pressure, which gives 98% pure helium; this second, high pressure stage is carried out separately from the main bulk of natural gas in order to avoid loss of helium in the liquefied residues, in which it is appreciably soluble. The purified helium is charged directly into cylinders at a pressure of 2,000 lb. per sq. in. The operating costs of the process in 1938 totalled \$12 per 1,000 cu. ft., or \$9 if allowance is made for the sale of by-product gas; it is stated that the costs could be reduced to \$5 by intensive production. The production of helium in the U.S.A. is now a Government monopoly. For further details, *see* Seibel, Ind. Eng. Chem. 1938, 30, 848.

Attempts to produce helium from natural gas on a commercial scale have also been made at Calgary, Alberta, using a process of cooling similar to that described above with a final purification by adsorption of impurities on charcoal (McLennan, J.C.S. 1920, 117, 923; Edwards and Elworthy, Proc. Roy. Soc. Canada, 1919, 13, III, 47; Lang, *ibid.* 1923, 17, III, 181; McLennan and Shrum, *ibid.* 1922, 16, III, 181; 1923, 17, III, 21). The distribution and production of helium in Canada are discussed by Rosewarne and Offord, Canada Dept. Mines Publ. 1932, No. 727, 42. Attempts were also made during the War of 1914–18 to obtain supplies of helium from the *soffioni* in Tuscany (Porlezza, Giorn. Chim. ind. appl. 1920, 2, 638, 687).

The separation of appreciable quantities of helium from air is difficult, as the content by volume is only about 1 part in 200,000. Owing to their low boiling points helium, neon and hydrogen are the last constituents of the atmosphere to condense on cooling. Dewar (Proc. Roy. Inst. 1903, 17, 223) has obtained a gas containing 50% of helium and neon by a condensation process working at normal pressures, using liquid hydrogen; this is impracticable on the commercial scale. Claude (Compt. rend. 1908, 147,

624) obtained a similar mixture, containing about 50% of helium and neon with 50% of nitrogen, as an uncondensable residue from a liquid-air plant. Regular supplies of this crude gas can be obtained from liquid-air rectification plants, which are a valuable source of the rare gases; a Claude plant produces some 20 litres of helium and neon per 1,000 cu. m. of air liquefied, small losses occurring through the solubility of helium in liquid nitrogen and oxygen. After removal of the nitrogen the helium-neon mixture contains about 25% of the former gas. The separation of helium and neon is particularly difficult on a large scale; for further details of the methods used, which have been described briefly above, see Ramsay and Travers, *Phil. Trans.* 1901, A. 197, 47; Crommelin, *Comm. Leiden*, No. 162c (1923); *Rec. trav. chim.* 1923, 42, 814; Meissner, *Naturwiss.* 1925, 13, 695. Natural gas is free from neon, so that pure helium can be obtained from this source without the difficult separation from neon, which is inevitable if the gases are obtained from the atmosphere.

#### PHYSICAL PROPERTIES OF HELIUM.

Helium is a colourless gas with a density of 0.17846 g. per litre at N.T.P., or 0.08923 g. per litre at 0°C. and 380 mm. (Baxter and Starkweather, *Proc. Nat. Acad. Sci.* 1926, 12, 20), giving a gram-molecular volume of 22.416 litres at N.T.P., in agreement with the results of other investigators. The molecular weight derived from the density data is 4.000, but as the gas is monatomic the accepted atomic weight gives the value 4.003. Isotherms of helium have been plotted by Onnes *et al.* at temperatures between -270° and 20° (*Comm. Leiden*, Nos. 164 (1923), 165c, 170a, 170b (1924), and 176b (1925); Abegg, *op. cit.* p. 376), Holborn and Otto (-258° to 400°) (*Z. Physik*, 1925, 33, 1; 1926, 38, 359), Wiebe, Gaddy and Heins (-70° to 200°, with pressures up to 1,000 atm.) (*J. Amer. Chem. Soc.* 1931, 53, 1721), and by other workers over smaller temperature ranges. Onnes represents the isotherms by an equation of the type:

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5}$$

where the "virial coefficients" A-F are constant at each temperature; in practice only A, B and C need be considered, the remaining terms being negligible. Values of these constants are given below:

Temp., °C.	A.	B × 10 <sup>3</sup> .	C × 10
0.00	0.99970	0.512	0.12
20.00	1.07273	0.534	0.13
100.35	1.36667	0.673	0.16

(*p* is in atmospheres, and *v* in multiples of the specific volume at N.T.P.). An equation of state used by Holborn and Otto, and Wiebe, Gaddy and Heins is of the type:

$$pv = A' + B'p + C'p^2 + D'p^3 + E'p^4$$

The latter authors give the following values of A', B' and C', expressing *pv* in Amagat units,

i.e. values of the ratio  $pv/p_0v_0$ , where  $p_0$  and  $v_0$  are the pressure and volume at N.T.P.:

Temp., °C.	A'.	B' × 10 <sup>4</sup> .	C' × 10 <sup>4</sup> .
-70	0.7438	5.322	4.332
-35	0.8721	5.296	4.336
0	1.00059	5.217	3.876
50	1.18480	5.1043	3.5308
100	1.3664	5.0442	3.4889
200	1.73284	4.7795	2.2518

As before, D' and E' are negligible. Jacyna, Derewjankin, Obnorsky and Parfentiev (*Bull. Acad. Polonaise*, 1934, A, 379) state that the following equation represents the behaviour of helium at -150° to 500° with considerable accuracy:

$$pv = RT - ap\{10T - T_0(1 - 11e^{b/T})\},$$

the constants having the following values: *a*,  $-1.085 \times 10^{-6}$ ; *b*,  $-6.85 \times 10^{-4}$ ;  $T_0$ , 273.22°; *R*, 211.82; the units are metres and kilograms. The fundamental coefficient of the normal helium thermometer, which determines the change of pressure of a quantity of helium on varying the temperature at constant volume, is 0.0036607 (Keesom, van der Horst and Taconis, *Physica*, 1934, 1, 324).

The viscosity coefficient of helium at 20° is  $1.941 \times 10^{-4}$  (Trautz and Binkele, *Ann. Physik*, 1930, [v], 5, 561; values are given for temperatures up to 200°). The variation of viscosity with temperature is given by:

$$\eta_1/\eta_2 = (T_1/T_2)^{0.66},$$

where  $\eta_1$  and  $\eta_2$  are the viscosities at the absolute temperatures  $T_1$  and  $T_2$ . Data for lower temperatures are given by van Itterbeek and Keesom (*Physica*, 1938, 5, 257). The viscosity of helium is independent of pressure except at pressures below about 2 mm.

According to Scheel and Heuse (*Ann. Physik*, 1913, [iv], 40, 473) the specific heat of helium at constant pressure is 5.040 g.-cal. per g.-mol. at 18°, and 4.980 at -180°; the ratio of the specific heats ( $\gamma$ ) is calculated to be 1.660, confirming that the gas is monatomic. Keesom and van Itterbeek find that the velocity of sound in helium gas at -182.9° is 559.1 metres per sec., giving  $\gamma$  1.661 at this temperature (*Proc. K. Akad. Wetensch. Amsterdam*, 1930, 33, 440; 1931, 34, 204). The thermal conductivity of helium at 0° is 0.0003365 g.-cal. per sq. cm. per sec. per °C. (Eucken, *Physikal. Z.* 1913, 14, 324); this value is for normal pressures, at which the variation of heat conductivity with pressure is negligible.

The refractive index of helium for the wavelength of the green mercury line ( $\lambda$  5461 Å.) is 1.00003489 (Cuthbertson and Cuthbertson, *Proc. Roy. Soc.* 1932, A, 135, 40; dispersion data are also given).

Helium is diamagnetic; its volume susceptibility is  $-0.780 \times 10^{-10}$  at N.T.P. (Hector, *Physical Rev.* 1924, [ii], 24, 418).

The dielectric constant of helium at N.T.P. is 1.000068 (Hochheim, *Verh. deut. physikal. Ges.* 1908, [ii], 10, 446).

The *arc spectrum* of helium contains two series of lines, the "orthohelium" and "parahelium" series; the discharge in a Geissler tube with a gas pressure of 3–5 mm. is orange-yellow in colour, and the orthohelium lines predominate. If the pressure is reduced or the discharge intensified the colour becomes greenish, the change corresponding with intensification of the parahelium lines; the wave-lengths of the principal lines in both series are given below (the wave-lengths are in Ångström units; the ortho- and para-helium series are denoted by O and P, respectively).

3888.64 O	4921.93 P
3964.73 P	5015.68 P
4026.19 O	5875.63 O
4120.81 O	6678.15 P
4387.93 P	7065.20 O
4471.48 O	7281.35 P
4713.15 O	

(Kayser, "Tabelle der Hauptlinien der Elemente," Berlin, 1926). A strong condensed discharge gives the so-called "spark" spectrum of helium (cf. Lyman, *Nature*, 1924, **113**, 785; *Astrophys. J.* 1924, **60**, 1).

Reference has been made above to the *diffusion* of helium through quartz glass at high temperatures. The results of numerous studies of the diffusion of helium through solids are somewhat inconclusive. The rate of diffusion through fused quartz at temperatures between  $-76^{\circ}$  and  $562^{\circ}$  is approximately proportional to the pressure, and inversely proportional to the thickness of the quartz diaphragm (Braaten and Clark, *J. Amer. Chem. Soc.* 1935, **57**, 2714). Lord Rayleigh (*Nature*, 1935, **135**, 30, 993; *Proc. Roy. Soc.* 1936, A, **156**, 350) records that helium passes freely through celluloid, gelatin and "cellophane" at room temperature; the gas is said to pass between constituent crystals of the solid. Single crystals of quartz and other substances are impermeable or only slightly permeable to helium. Lord Rayleigh supports the view that the transmission of helium through vitreous quartz, boron trioxide, etc., is due to creepage of the gas molecules along sub-microscopic channels in the structure; addition of alkali to the glass closes the channels at room temperature and prevents diffusion of the gas. Taylor and Rast conclude, however, that diffusion of helium through Pyrex glass is governed by chemical factors (*J. Chem. Physics*, 1938, **6**, 612).

The Ostwald coefficients for the *solubility* of helium in water are as follows:

Temperature	$0^{\circ}$	$10^{\circ}$	$20^{\circ}$	$30^{\circ}$ C.
Ostwald coeff.	0.00955	0.0093	0.0091	0.0090

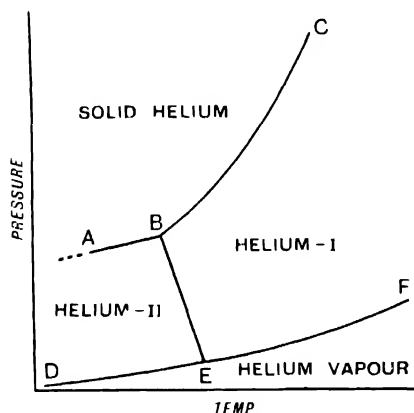
(The corresponding Bunsen coefficients are 0.00955, 0.00895, 0.0085 and 0.0081, respectively) (cf. Cady, Elsey and Berger, *J. Amer. Chem. Soc.* 1922, **44**, 1456, and a correction by Valentiner, *Z. Physik*, 1930, **61**, 563). Wiebe and Gaddy (*J. Amer. Chem. Soc.* 1935, **57**, 847) have determined the solubility in water at  $0-75^{\circ}$ , with gas pressures up to 1,000 atmospheres.

**Critical Constants of Helium; Liquefaction of Helium.**—The critical temperature of helium is  $-268.0^{\circ}$  ( $5.1^{\circ}$  abs.), and the critical pressure is 2.3 atmospheres. At normal temperatures the Joule-Thompson effect for helium (for measurements, see Roebuck and Osterberg, *Physical Rev.* 1933, [ii], **43**, 60) is opposite in sign to that for most gases, and helium is heated on expansion through a jet or porous plug; the usual methods of cooling used in gas liquefiers (cf. LIQUEFACTION OF GASES) cannot be applied for this reason. In addition, the critical temperature is extremely low, so that helium cannot be liquefied by application of pressure at any readily available temperature. In 1908 Onnes found that the Joule-Thompson effect for helium was reversed by cooling the gas in solid hydrogen, and was able to use the effect to produce further cooling, and eventually liquefaction of the helium (*Compt. rend.* 1908, **147**, 421; *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **11**, 68). An apparatus for the continuous production of liquid helium is described by Onnes (*Versl. Akad. Amsterdam*, 1926, **35**, 862; *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 1176). Cooling is effected on the cascade principle, temperatures of  $-85^{\circ}$ ,  $-150^{\circ}$ ,  $-183^{\circ}$  and  $-253^{\circ}$  being reached by evaporation of liquefied methyl chloride, ethylene, oxygen and hydrogen, respectively, in successive cycles. The helium is compressed to 30 atm. pressure, cooled to  $-253^{\circ}$ , and expanded through a jet; this process, proceeding continuously, ultimately causes liquefaction of the helium. For descriptions of other liquid-helium plants, see Landemann and Keeley, *Nature*, 1933, **131**, 191, and Kapitza, *Proc. Roy. Soc.* 1934, A, **147**, 189. Kapitza's apparatus does not require liquid hydrogen for its operation. Pre-cooling with liquid nitrogen is found to suffice, further cooling of the helium to about  $10^{\circ}$  abs. being produced by a small expansion engine incorporated in the apparatus; the final liquefaction depends on the Joule-Thompson effect. The apparatus produces liquid helium  $1\frac{1}{2}$  hours after starting, and the output is 2 litres per hour, with a liquid nitrogen consumption of  $1\frac{1}{2}$  litres per litre of liquid helium.

The *boiling point* of liquid helium under 760 mm. pressure is  $4.216^{\circ}$  abs. (Schmidt and Keesom, *Physica*, 1937, **4**, 963). Data for the *vapour pressure* over the range 0–760 mm. are given by the same authors (*ibid.* 1937, **4**, 971). The *density* of liquid helium at the normal boiling-point is 0.122 g. per c.c., giving a *molecular volume* of 31.9 c.c. The *compressibility*,  $7$  to  $8 \times 10^{-3}$  sq. cm. per kg., is the highest of any known liquid (Keesom and Clusius, *Proc. K. Akad. Wetensch. Amsterdam*, 1932, **35**, 320). The *latent heat of vaporisation* has a broad maximum in the neighbourhood of  $3^{\circ}$  (approx. 5.6 g.-cal. per g.), and falls rapidly at higher temperatures (Dana and Onnes, *ibid.* 1926, **29**, 1051; Van Laar, *ibid.* 1926, **29**, 1017).

Liquid helium is one of the most remarkable substances known to chemists; it exists in two distinct forms, known as helium-I and helium-II. The relationships between these two liquid forms and the vapour and solid are illustrated dia-

grammatically in the curve below, which is not to scale. Liquid helium exists as helium-I at normal pressures; the liquid, which can be kept for short periods in a good Dewar vessel, is almost invisible, but the surface has a similar appearance to a sheet of mica by reflected light. Slow boiling produces a stream of bubbles of helium vapour rising through the liquid. If the pressure over the liquid is reduced to a point in the curve DE immediate transformation to helium-II takes place; the only visible evidence of a change is the sudden cessation of the stream of bubbles as the point E is passed. The point E, commonly known as the  $\lambda$ -point, is the triple point at which helium-I, helium-II and the vapour coexist in equilibrium; it corresponds with a temperature of 2.186° abs. and a vapour pressure of 3.83 cm. (Schmidt and Keesom, *Physica*, 1937, 4, 971). The line EB (the " $\lambda$ -line") represents the variation of the  $\lambda$ -point



with change of pressure. The  $\lambda$ -point corresponds with a sharp maximum in the specific heat of liquid helium (Keesom and Clusius, *Proc. K. Akad. Wetensch. Amsterdam*, 1932, 35, 307), but there is apparently no latent heat associated with the transition between the two forms. The density of the liquid at various pressures reaches a maximum value along the  $\lambda$ -line (Keesom and Keesom, *Physica*, 1933-34, 1, 128). The viscosity falls rapidly below the  $\lambda$ -point, and the viscosity of helium-II at low temperatures is remarkably low (e.g. 1.24 micropoises at 1.304° abs.; water at 20° has a viscosity of about 10,000 micropoises) (cf. Keesom and Macwood, *Physica*, 1938, 5, 737). The thermal conductivity of liquid helium also shows a remarkable change at the  $\lambda$ -point; it rises from  $6 \times 10^{-5}$  g.-cal. per sq. cm. per sec. per °C. at 3.3° abs. (helium-I) to 190 (same units) at 1.4-1.75° abs. (helium-II). Helium-II is by far the best conductor of heat yet discovered. Helium-II also has remarkable capillary properties; it forms a film about  $5 \times 10^{-6}$  cm. thick on any solid with which it comes into contact, and the liquid is transferred through this film to the lowest available level (Daunt and Mendelssohn, *Nature*, 1938, 141, 911; 142A, 475). No discontinuity occurs in the surface tension of liquid

helium at the  $\lambda$ -point (Allen and Misener, *Proc. Camb. Phil. Soc.* 1938, 34, 299), and the molecular refractions of the two liquid forms are equal (Johns and Wilhelm, *Canad. J. Res.* 1938, A, 16, 131). Debye-Scherrer X-ray diagrams of helium-I and -II have been obtained by Keesom and Taconis (*Physica*, 1938, 5, 270), who consider that the latter has a partly ordered lattice structure based on a face-centred cubic arrangement, but with half the atoms missing, leaving channels in the structure. The degree of order in the structure of helium-II is thus less than that in the solid, but greater than that in helium-I.

The portions DE and EF of the curves represent the vapour pressures of helium-II and -I, respectively. These vapour pressures ( $p$ , in cm.) are given by the following equations:

Helium-I:

$$\log_{10} p = 1.217 - 3.024/T + 2.208 \log_{10} T.$$

Helium-II:

$$\log_{10} p = 2.035 - 3.859/T + 0.922 \log_{10} T.$$

(Keesom *et al.*, *Proc. K. Akad. Wetensch. Amsterdam*, 1929, 32, 864, 1314). The point B represents the triple point for solid helium, helium-I, and helium-II, at 1.753° abs. and 29.91 atm. pressure. Solid helium is obtained only by compression of one of the liquid forms; the solid, liquid and vapour cannot coexist in equilibrium. Solidification of helium is accompanied by little change in appearance, and is detected experimentally by the freezing up of a mechanical stirrer. Even at the absolute zero of temperature, solid helium would not be stable at pressures less than about 25 atm. (Keesom, *Physica*, 1934, 1, 128, 161; Kaishew and Simon, *Nature*, 1934, 133, 460; Simon, *ibid.* 1934, 133, 529). The density of solid helium in equilibrium with liquid helium-I is 0.23 at 4.0° and 0.22 at 3.6° abs.; the heat of fusion is 6.75 g.-cal. per g.-atom at 4.0°, and 5.1 g.-cal. at 3.4° abs. (Kaishew and Simon, *loc. cit.*). The melting-point curve BC, over the range 12-42° abs., is given by the equation:

$$\log_{10}(p+17) = 1.5544 \log_{10} T + 1.236;$$

$p$  is expressed in kg. per sq. cm. (Simon, Ruhemann and Edwards, *Z. physikal. Chem.* 1929, B, 2, 340; 6, 62). According to Keesom and Taconis (*Proc. K. Akad. Wetensch. Amsterdam*, 1938, 41, 95), solid helium at 1.45° abs. and 37 atm. pressure has a hexagonal close-packed structure; there are two atoms in the unit cell, 3.57 Å. apart, and the spacings of the {100} and {101} planes are 3.07 and 2.75 Å., respectively.

For general accounts of the physics of solid and liquid helium, see Satterly, *Rev. Mod. Physics*, 1936, 8, 347; Keesom, *Natuurwetensch. Tijds.* 1929, 11, 65; and Burton, Smith and Wilhelm, "Phenomena at the Temperature of Liquid Helium," New York, 1940.

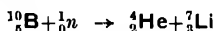
#### CHEMICAL PROPERTIES OF HELIUM.

There is little evidence for the existence of well-defined stoichiometric compounds of helium, although a number of solid substances of indefinite composition containing helium have been obtained, generally under the action of an

electric discharge. Intense electron bombardment of helium in the neighbourhood of a tungsten filament gives a black substance which Boomer (Proc. Roy. Soc. 1925, A, 109, 198; Nature, 1925, 115, 16) considered to be a tungsten helide  $WHe_2$ . Boomer also found indications of the existence of compounds with mercury, iodine, phosphorus and sulphur. Damianovitch (*cf.* a review covering the question of the formation of helium compounds, Bull. Soc. chim. 1938, [v], 5, 1085, 1092, 1106) has also obtained a supposed compound of helium and platinum. There is no evidence for the formation of hydrates, or of compounds with boron trifluoride similar to those given by argon.

#### HELIUM AND RADIOACTIVITY.

The  $\alpha$ -rays produced in radioactive processes consist of the nuclei of helium atoms, which become neutral helium atoms after regaining two electrons apiece. One gram of radium in equilibrium with its disintegration products yields 167 cu. mm. of helium per year. The production of helium in the disintegration of radioactive elements has been confirmed experimentally in a number of cases (Abegg, *op. cit.* p. 173). The helium produced in the "artificial" nuclear reaction



has also been collected and determined by Paneth, Glückauf and Lolcit (Proc. Roy. Soc. 1936, A, 157, 412).

Attempts have been made to obtain the helium isotopes  $^3He$  and  $^5He$  by artificial disintegration methods. Evidence has been obtained for the production of  $^3He$  from deuterium in a mass-spectrograph (Bleakney, Harnwell, Lozier, Smith and Smyth, Physical Rev. 1934, [iii], 46, 81) and Joliot and Zlotowski (Compt. rend. 1938, 206, 1256) state that  $^5He$  is formed with protons during  $\alpha$ -particle bombardment of paraffin wax ( $^4_2He + ^1_1H \rightarrow ^5_2He + ^1_1H$ ). For a general discussion of the question, see Lord Rutherford, Nature, 1937, 140, 303.

#### DETECTION AND DETERMINATION OF HELIUM.

Helium is invariably detected by its characteristic spectrum (*see above*), given by a discharge through the gas in a Geissler tube. This method has been refined by Paneth and Peters (Z. physikal. Chem. 1928, 134, 353) to permit detection of  $10^{-10}$  c.c. of the gas; the lines at 5875.63 and 5015.68 Å. are the last to disappear from the spectrum when the quantity of helium present in the discharge is reduced.

The determination of helium in gas mixtures, in the absence of other inert gases, is carried out by volume measurement after removing all other gases by adsorption on charcoal, as in McLennan's apparatus for the determination of helium in natural gases (J.C.S. 1920, 117, 943), or by chemical means (*see, for instance*, Moureu, J. Chim. phys. 1913, 11, 63). If other rare gases are present the determination is more difficult, but gases other than helium and neon can be removed by fractional adsorption (Moureu, *l.c.*) and the helium-neon mixture analysed by the method of Paneth and Urry (Mikrochem.,

Emich Festschrift, 1930, 233), which employs a hot-wire manometer in a Wheatstone bridge circuit. This method can be used with gas pressures as low as  $6 \times 10^{-6}$  mm. A similar method can be used for the determination of  $7 \times 10^{-9}$  to  $10^{-4}$  c.c. of pure helium, with an error of about 1% for the larger of these volumes. Schröer (Z. anal. Chem. 1937, 111, 161) and Germann, Gagos and Neilson (Ind. Eng. Chem. [Anal.], 1934, 6, 215) have described methods for the determination of helium in gas mixtures.

#### USES OF HELIUM.

Large quantities of helium have been used for filling balloons and dirigibles; helium has 92% of the lifting power of hydrogen, and has the overwhelming advantage of complete non-inflammability. In addition, the loss of gas by diffusion through the envelope is smaller with helium than with hydrogen. Up to 26% of hydrogen may be mixed with the helium without producing an inflammable mixture (Satterly and Burton, Trans. Roy. Soc. Canada, 1919, 13, 111, 211; Ledig, J. Ind. Eng. Chem. 1920, 12, 1098).

Increasing amounts of helium are now being used for medical purposes. It is of great value in certain types of respiratory obstruction, as a mixture containing 79% of helium and 21% of oxygen (corresponding with air in composition) is much easier to breathe than air, minimising muscular effort (Sykes and Lawrence, Brit. Med. J. 1938, ii, 448). Substitution of helium for the nitrogen in the air supply to divers reduces their liability to "divers' bends," a complaint caused by separation of nitrogen from the blood on reduction of pressure. "Decompression" of cases of "bends" is much more rapidly effected with helium and oxygen than with air (End, Amer. J. Physiol. 1937, 120, 712). Helium has also been used for pneumothorax fillings (Klin. Woch. 1938, 17, 1153).

In the laboratory liquid helium is extensively used in low temperature physics. Temperatures less than  $1^\circ$  abs. can be reached by evaporation of the liquid under reduced pressure. The helium vapour-pressure thermometer is also useful in the same field. The helium gas thermometer is the basis of the International helium scale of temperature.

Owing to the simplicity of the helium molecule, helium has been made the subject of numerous studies in molecular and atomic physics, which are outside the scope of this article; reference should be made to the Indexes of one of the Abstract Journals. A full account of the work done on the chemistry of helium up to 1927 is included in Abegg's "Handbuch der anorganischen Chemie," Vol. IV, Section 3, Part 1, "Die Edelgase."

A. J. E. W.

"HELLA" BUSHLIGHT (v. Vol. V, 486d).

**HELLANDITE.** Silicate of yttrium, erbium, calcium, aluminium and manganese crystallised in the monoclinic system. One analysis showed  $Y_2O_3$  19.29,  $Er_2O_3$  15.43,  $Ca_2O_3$  1.01%. The crystals are prismatic in habit, and when fresh are nut-brown in colour with a resinous lustre on the conchoidal fracture. Sp.gr. 3.70; hardness  $5\frac{1}{2}$ . The mineral is readily soluble in hydrochloric acid with evolution of chlorine, and

it is fusible in the Bunsen flame. Usually, however, it is much altered to a yellow or white earthy material which is optically isotropic and contains much water. The crystals are found singly, in association with tourmaline, apatite, thorite, orthite, etc., embedded in the granite pegmatite-veins which are quarried for felspar in the neighbourhood of Kragero in the south of Norway.

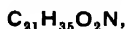
L. J. S.

**HELLEBOREIN, HELLEBORIN, HELLEBRIN** (v. Vol. II, 387b, c).

**HELLEBORUS.** In ancient Greek medicine *ἑλλέβορος* was a drug prescribed for mania. The Black Hellebore of Theophrastus ("Enquiry into Plants," trans. A. Hort, London, 1916, II, 266) has been identified by Thiselton-Dyer as *Helleborus cyclophyllus* Boiss., and the Greeks' White Hellebore was considered by the same authority to have been *Veratrum album* L. The Romans (Celsus, c. A.D. 10) administered *V. album* under the name Helleborus. The confusion of *H. species* (Fam. Ranunculaceae) and *V. species* (Fam. Liliaceae) continued in later centuries (cf. Gerard's "Herball," 1597) until the present day. Thus Green Hellebore, *H. viridis*; Stinking Hellebore, *H. fatidus*; and Black Hellebore, *H. niger*, have been traditional remedies in England, but none of these drugs is included in the British Pharmacopœia, 1932. In the United States, however, Green Hellebore, a native swamp plant, *V. viride*, is official in U.S. Pharmacopœia XI; White Hellebore is *V. album*, a closely related substitute imported from Europe but not officially recognised. The risk of confusing true Hellebores with Veratrum species is pointed out in the literature (e.g. Henry, "Plant Alkaloids," 3rd ed., 1939, p. 629; "Extra Pharmacopœia," 1941, I, p. 364; B.P.C. 1934, 505).

*H. niger*, Christmas Rose (v. Vol. II, 1). For the active cardiac glycosides recently isolated, see Vol. II, 387b. The drug is the root and rhizome. The powdered root is irritant and sternutatory; given internally it is strongly cathartic, and toxic, over doses have had fatal results. *H. niger* does not contain alkaloids (Keller and Schöbel, Arch. Pharm. 1927, 265, 1238). For further references, see J. L. L. van Rijn, "Die Glykoside," 2nd ed., Berlin, 1931, pp. 128, 132, 133; "U.S. Dispensatory," 22nd ed., 1937, p. 1406.

*Helleborus viridis*, Green Hellebore, Fam. Ranunculaceae, is found as a rare wild flower in England and was a traditional remedy for dropsy (Sowerby, "English Botany," 1873, Vol. I, p. 56). A continental variety contained the glycosides previously found in *H. niger* and in addition four alkaloids: *celliamine*,



m.p. 127–131°; *sprintillamine*,  $\text{C}_{28}\text{H}_{45}\text{O}_4\text{N}$ , m.p. 228–229°; *sprintilline*,  $\text{C}_{25}\text{H}_{41}\text{O}_3\text{N}$ , m.p. 141–142°, which are cardiac alkaloids, and *alkaloid V*,  $\text{C}_{35}\text{H}_{43}\text{O}_6\text{N}$ , m.p. 267–268° (Keller and Schöbel, l.c.; *ibid.* 1928, 266, 545). The three named alkaloids are pharmacologically similar and resemble cevadine, aconitine and delphinine (Franzen, Arch. exp. Path. Pharm. 1931, 159, 183). For a comparison of the

potency of six *Helleborus species*, see Tschirch, "Handb. d. Pharmakognosie," 2nd ed., Vol. II. Berger discussed characteristics and tests for the black and green species (Scientia Pharm. 1939, 10, 83). The rhizomes of these species cannot be distinguished unless the radical leaves are still attached (Wallis and Saunders, Pharm. J. 1924, 113, 90, 133).

*H. fatidus* (Sowerby, *op. cit.*), formerly a reputed antihelminthic. *H. orientalis* has been analysed by Sonntag and Kuhlmann (Apoth.-Ztg. 1937, 52, 227; see also papers in Pharm. Ztg. 1937, 82).

**White Hellebore.**—*Veratrum album* (Fam. Liliaceae). The drug is the dried rhizome and root of a European alpine plant; it is not official in the British Pharmacopœia or in U.S. Pharmacopœia XI, and is classed in Part I of the (British) Poisons List. *V. album* was formerly prescribed as a cardiac depressant. Its toxicity is best determined by a bio-assay, e.g. on *Daphnia magna* (Viehoever and Cohen, Amer. J. Pharm. 1939, 111, 86). The powdered drug has been used as a parasiticide. In appearance and properties *V. album* so closely resembles *V. viride* that some authors considered the drugs to be equivalent. The alkaloids of *V. album* have been studied by Wright and Luff (J.C.S. 1879, 35, 405) and by Salzberger (Arch. Pharm. 1890, 228, 462) and recently Poethke (*ibid.* 1937, 275, 357, 571; 1938, 276, 170; Amer. Chem. Abstr. 1939, 33, 807) has revised the existing data and described some new alkaloids. Those now known include *jervine*,  $\text{C}_{28}\text{H}_{37}\text{O}_3\text{N}$ , m.p. 243°; *rubijervine*,  $\text{C}_{26}\text{H}_{43}\text{O}_2\text{N}$ , m.p. 239°; *pseudojervine*,  $\text{C}_{35}\text{H}_{45}\text{O}_8\text{N}$ , m.p. 304°; *protoveratrine*,  $\text{C}_{40}\text{H}_{63}\text{O}_{14}\text{N}$ , m.p. 255°; and *germerine*,  $\text{C}_{36}\text{H}_{57}\text{O}_{11}\text{N}$ , m.p. 193°. These are crystalline, and protoveratrine is highly toxic; see also Henry, *op. cit.*, p. 629.

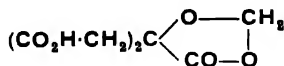
**Green Hellebore, American Hellebore.**—*Veratrum viride* (Fam. Liliaceae), cf. White Hellebore above. The drug is official in the U.S. Pharmacopœia XI, but not in the British Pharmacopœia; it is classed in Part I of the (British) Poisons List. It has been prescribed as a powerful cardiac sedative. For its standardisation, see *V. album*. It has been largely used in dilute aqueous suspension for destroying insect larvae in garbage, but its toxic properties render it dangerous for spraying vegetables. The alkaloidal content resembles that of *V. album* but has not been so closely studied; the presence of cevadine has been reported in *V. viride* (Wright, J.C.S. 1879, 35, 422; cf. T. Sollman, "Pharmacology," 5th ed., Philadelphia, 1936).

J. N. G.

**HELLHOFFITE** (v. Vol. IV, 545d).

**HELMINTHOSPORIN** (v. Vol. V, 55a).

"**HELMITOL**," "formamol." Trade name for a compound prepared from hexamethylenetetramine by the action of anhydromethylene citric acid,



obtained by the interaction of formaldehyde or chloromethyl alcohol and citric acid (G.P.



129255, 150949). It is valued as a urinary antiseptic and is used in the treatment of rheumatism.

**HELVITE** (v. Vol. III, 547a).

**HEMELLITHENOL.** 3:4:5-Trimethylphenol, m.p. 81°. (Jacobsen, Ber. 1886, 19, 2518).

**HEMICELLULOSES.** The cell-walls of many plants contain polysaccharides other than cellulose, certain of which have been described by the general name of "hemicellulose." The term was suggested by E. Schulze in 1892 to embrace certain polysaccharides which he obtained from plant materials by extraction with dilute alkali. Since that time the name has been given to polysaccharides of the cell-wall which are soluble in alkali and hydrolysed readily by dilute acid. It is obvious that by this definition a large number of carbohydrates with no significant constitutional relationship will be included, and in practice the term is retained, only because of its convenience for referring in general to the complex mixture of polysaccharides obtained when plant material is extracted with alkali. Homogeneous products isolated from such a mixture are usually named from the  $C_4$ ,  $C_5$  sugar they yield on hydrolysis, e.g. xylan from esparto grass, mannan from the ivory-nut. For convenience, these substances are described under CARBOHYDRATES, Vol. II, 287a, 303c.

The difficult task of preparing pure homogeneous specimens from hemicellulose material has been accomplished in comparatively few cases. Most workers partly purify their products by fractional precipitation (e.g. by acidification of the alkaline extract, and by the addition of alcohol) or by forming an insoluble copper complex (Heuser, J. pr. Chem. 1922, [ii], 104, 261), but this process rarely yields pure products. Separation may sometimes be effected by methylation (see Hampton, Haworth and Hirst, J.C.S., 1929, 1739).

A brief note on the hemicelluloses isolated from the chief sources follows.

**Wood.**—The hemicellulose from American white oak gives on hydrolysis *d*-xylose, *l*-arabinose, *d*-mannose and *d*-galactose (O'Dwyer, Biochem. J. 1923, 17, 503). English oak has also been examined by O'Dwyer (*ibid.* 1939, 33, 713; 1940, 34, 149). Two main fractions of the hemicellulose have been obtained; A, by acidification of the alkaline extract, and B, by addition of alcohol to the filtrate from this operation. "Hemicellulose A" from both the sapwood and the heartwood contains xylose and a methy uronic acid, but that from the sapwood contains also some 10% of glucose. "Hemicellulose B" from both sources contains xylose and a uronic acid, and that from sapwood contains glucose in addition.

Boxwood yields a product from which xylose and a uronic acid have been isolated (Preece, *ibid.*, 1931, 25, 1304). From larch wood (*Larix occidentalis*) an "ε-galactan" has been obtained which has been separated into a galactan and an araban (Peterson, Barry, Unkauf and Wise, J. Amer. Chem. Soc. 1940, 62, 2361; Hirst, Jones and Campbell, Nature, 1941, 147, 25). The molecular weights of several polysaccharides from wood have been calculated by Husemann from

osmotic pressure measurements (Naturwiss. 1939, 27, 595).

**Straw.**—From oat and rye straw hemicelluloses have been obtained which on hydrolysis yield *d*-xylose, *l*-arabinose and *d*-galactose (Norman, Biochem. J. 1929, 23, 1353). Those from wheat straw and lucerne hay yield chiefly *d*-xylose and *l*-arabinose (Weihe and Phillips, J. Agric. Res. 1940, 60, 781; Phillips and Davis, *ibid.* 1940, 60, 775).

**Seeds.**—*d*-Xylose, *l*-arabinose, *d*-glucose and uronic acids have been found on hydrolysis of the hemicellulose from wheat bran (Norris and Preece, Biochem. J. 1930, 24, 60), and maize cobs give somewhat similar products (Preece, *ibid.* 1930, 24, 973; Angell and Norris, *ibid.* 1936, 30, 2155). From the shell of the ivory-nut (*Phytalephas macrocarpa*) mannans have been isolated (Patterson, J.C.S. 1923, 1139; Klages, Annalen, 1934, 509, 159). From the peanut (*Arachis hypogaea*) a galactan and an araban have been obtained, and it appears that the structure of the latter is similar to that of the araban present in apple pomace (Hirst and Jones, J.C.S. 1938, 496; 1939, 454).

For a discussion of the many problems in this field, see A. G. Norman, "The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.," Oxford University Press, 1937. For experimental details of the methods used in these investigations and a description of the isolation of many hemicelluloses, see Dorée, "The Methods of Cellulose Chemistry," Chapman and Hall, 1933.

G. T. Y.

**HEMIMELLITENE** (v. Vol. III, 457a).

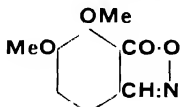
**HEMIMORPHITE** (or Electric Calamine).

Hydrous silicate of zinc,  $Zn_2H_2SiO_5$ , crystallising in the orthorhombic system, and an important ore of zinc. The water is expelled only at a red heat, and the formula may be written as an acid salt or as a basic metasilicate,  $Zn_2(OH)_2SiO_3$ , or as a basic diorthosilicate,  $H_2Zn_2(ZnOH)_2(SiO_3)_2$ . An important chemical character, of help in recognising the mineral, is the fact that it readily gelatinises with acids. Crystals are not uncommon, but are usually small; they are often grouped in fan-like aggregates, at the edges of which the perfect prismatic cleavage with pearly lustre may often be seen. When doubly terminated, they show a characteristic hemimorphic development, different kinds of faces being present at the two ends of the vertical axis. Connected with this polarity is the strong pyroelectric character of the crystals. The mineral also forms mamillated and stalactitic masses; or it may be massive and cavernous and cellular, being then often mixed with clayey matter or smithsonite. The colour ranges from white to yellow and brown, and is sometimes bright blue or green. Sp.gr. 3.45; hardness 4–5. Hemimorphite usually occurs in association with zinc carbonate (smithsonite) and zinc-blende and ores of lead, often as veins and beds in limestone strata. Fine large crystals are found at Santa Eulalia, Chihuahua, Mexico; and the mineral has been mined as an ore at several localities, e.g. Cumberland, Altenberg in Rhenish Prussia, Sardinia, Santander in Spain, Hungary, Northern

Rhodesia, United States, British Columbia, etc. The ambiguous name calamine (*q.v.*) is often applied to this mineral species.

L. J. S.

**HEMIPINIC ACID**,  $C_{10}H_{10}O_6$  (3:4-dimethoxyphthalic acid, 3:4-dimethoxybenzene-1:2-dicarboxylic acid) is a product of oxidation of many alkaloids, *e.g.* narcotine (Wöhler, *Annalen*, 1844, 50, 17), berberine (Schmidt, *Ber.* 1883, 16, 2589). It may be prepared by warming 3:4-dimethoxy-2-methylbenzoic acid with alkaline permanganate (Perkin, *J.C.S.* 1916, 109, 921), or by heating Liebermann's opianic acid oxime anhydride (*Ber.* 1880, 19, 2278),



with potassium hydroxide, acidifying and extracting with ether (Goldschmidt, *Monatsh.* 1888, 9, 376). The melting-point varies with the rate of heating, 177° (Perkin, *J.C.S.* 1889, 55, 73, 85), 186–188° (Rabe and McMillan, *Annalen*, 1910, 377, 239, 241). It crystallises with  $2H_2O$  usually, but also with 1 mol. and  $2\frac{1}{2}$  mol. of water.

Slightly soluble in cold water, but more so than opianic acid, from which it may be separated by means of its calcium salt (Rodionow and Abletsova, *Chem. Zentr.* 1935, 11, 685). Soluble in alcohol but sparingly soluble in ether. Heat of combustion 102.46 g.-cal. (Leroy, *Compt. rend.* 1900, 130, 510),  $K = 1.1 \times 10^{-3}$  at 25° (Karpal, *Monatsh.* 1897, 18, 462). The aqueous solution gives an orange-yellow precipitate with ferric chloride solution. Lead acetate gives a gelatinous precipitate soluble in excess of the reagent and reprecipitated as a dense powder on heating.

On heating at 180° for 1 hour the *anhydride* is formed (Beckett and Wright, *J.C.S.* 1876, 29, 173, 282). The anhydride is also obtained by the action of 4 mol. phosphorus pentachloride on the dried acid at 140° for 2 hours in sealed tubes (Freund and Horst, *Ber.* 1894, 27, 333). The anhydride, m.p. 166–167°, reacts with resorcinol forming dimethoxyfluorescein (Friedl, Weizmann and Wyler, *J.C.S.* 1907, 91, 1584).

Gentle nitration gives 6-nitrohemipinic acid, m.p. 154–155°, and 6-nitro-2:3-dimethoxybenzoic acid, m.p. 189° (Wegscheider and von Rušnov, *Monatsh.* 1908, 29, 546; Wegscheider and Klemenc, *ibid.* 1910, 31, 740), while fuming nitric acid at 60° gives, amongst other products, 5:6-dinitro-2:3-dimethoxybenzoic acid, m.p. 196–197° (Wegscheider and Klemenc, *l.c.*).

Heating with concentrated sulphuric acid gives 1:2:5:6-tetrahydroxyanthraquinone (Liebermann and Chojnaeki, *Annalen*, 1872, 162, 327).

5-Chlorohemipinic acid, m.p. 168–169°, is obtained from the acid and potassium hypochlorite in caustic potash solution. 5:6-Dichlorohemipinic acid, m.p. 130°, is obtained by the direct chlorination of an alkaline solution of the acid (Faltis, Wrann and Kuhns, *Annalen*, 1932, 497, 88).

For 6-amino-, 6-hydroxy-, 6-chloro- and 6-iodohemipinic acids, see Grunc, *Ber.* 1886, 19, 2302; Faltis and Kleiber, *Monatsh.* 1929, 53/54, 620.

The acid forms many esters, both mono- and di-esters. The 2-monomethyl ester exists in two modifications; the labile form crystallises from water with  $1H_2O$ , m.p. 96–98°, anhydrous 121–122°; the stable form with  $1H_2O$  crystallises from ether, m.p. 98–102°, water-free crystals 138° (Wegscheider, *Monatsh.* 1897, 18, 418, 589, 629).

Hemipinic anhydride condenses with *o*-cresol in the presence of  $AlCl_3$  to give 3:4-dimethoxy-2:2-di(4-hydroxy-3-methylphenyl) phthalide and 3:4-dimethoxy-2-(2-hydroxy-3-methylbenzoyl)-benzoic acid (Jacobson and Adams, *J. Amer. Chem. Soc.* 1925, 47, 283).

*m*-Hemipinic Acid (4:5-dimethoxybenzene-1:2-dicarboxylic acid).—Obtained by the degradational oxidation of alkaloids such as papaverine (Goldschmidt, *Monatsh.* 1885, 6, 380) or corydalin (Dobbie and Marsden, *J.C.S.* 1897, 71, 664), also by oxidation of brazilin trimethyl ether (Gilbody, Perkin and Gates, *ibid.* 1901, 79, 1405) and of emetin (Windaus and Hermanns, *Ber.* 1914, 47, 1471; *cf.* Späth and Leithe, *ibid.* 1927, 60, 13, 688).

The acid may be prepared by the alkaline oxidation of 4:5-dimethoxy-2-methylbenzoic acid with potassium permanganate (Luff, Perkin and Robinson, *J.C.S.* 1910, 99, 1136), or by condensation of 3:4-dimethoxybenzoic acid with chloral and sulphuric acid followed by reduction to 3:4-dimethoxy-6- $\beta$ -dichloroethylbenzoic acid, and oxidation to *m*-hemipinic acid with alkaline permanganate (Meldrum and Parikh, *Chem. Zentr.* 1935, II, 213). It may also be prepared by the oxidation of 5:6-dimethoxy-1-hydrindone with nitric acid (Perkin and Robinson, *J.C.S.* 1907, 91, 1083).

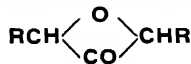
*m*-Hemipinic acid crystallises with 1 and 2 mol. of water, and also in the anhydrous form; m.p. (gradual heating) 174–175°, (more rapid heating) 179–182°; yields the *anhydride*, m.p. 175°, on heating above 190°. The acid is much less soluble in water than the isomeric acid and gives a cinnamon-orange precipitate with ferric chloride and a white precipitate with silver nitrate. Nitric acid gives dinitroveratrol, and 4:5-dihydroxyphthalic acid is obtained by hydrolysis with hydriodic acid (Rossin, *Monatsh.* 1891, 12, 493). The acid may be identified by means of its *ethylimide*, m.p. 229–230°, and by the *anhydride*.

*iso*Hemipinic acid (3:4-dimethoxybenzene-1:5-dicarboxylic acid), has been isolated from lignins (Freudenberg, Janson, Knopf, Haag and Meister, *Ber.* 1936, 69, 1415).

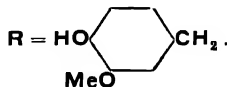
**HEMISINE.** Syn. for Adrenaline (*q.v.*).

**HEMLOCK** (*v.* Vol. III, 324c).

**HEMLOCK SPRUCE RESIN.** The main constituent of the resin, *e.g.* from *Picea excelsa* and from the Japanese hemlock (Kawamura, *Bull. Imp. Forestry Exp. Stat. Tokyo*, 1932, No. 31, 73) is *tsugaresinol*, m.p. 235–237°,  $C_{20}H_{20}O_6$ . Its structure is given as:



where



**HEMP** (v. Vol. V, 162c-163c).

**HEMPSEED OIL.** The seeds of the hemp plant, *Cannabis sativa* L., contain about 30% of oil, of which the bulk can be removed by expression. Hemp is cultivated in most warm and temperate lands, either for the sake of the fibre or as a source of oil. The chief producers of the oil, which is mainly consumed locally, although the expressed hempseed cake appears in international trade, are China (Manchuria), Russia, France and Italy; the Russian production of 530,000 to 956,000 tons per annum over the years 1925-30 equalling that of linseed oil. The annual French production of oil has been estimated at over 10,000 tons, whilst a similar amount has been forecast for Germany. The cultivation of hemp has also been undertaken of late years in the United States, where appreciation of the oil as a raw material for the paint and varnish industry has been steadily growing.

Freshly expressed hempseed oil is light green to greenish-yellow in colour, becoming brownish-yellow on keeping, and is readily refined. The chemical and physical characteristics of the oil fall within the following ranges:  $d_{15}^{20}$  0.925-0.933; saponification value 188-194; iodine value 140-170 (usually between 150 and 166); m.p. of fatty acids 17-21°C. Sprinkmeyer and Diedrichs (Z. Unters. Nahr.-u. Genussm. 1912, **23**, 679) obtained 8.8% of ether-insoluble bromides by brominating the oil itself; Eibner (cf. Eibner and Wibelitz, Chem. Umschau, 1924, **31**, 123) obtained only 2% of ether-insoluble bromides from the fatty acids of hemp oil, but Heiduschka and Zwergal (Pharm. Zentralh. 1936, **77**, 551) and Kaufmann and Juschkevitch (Z. angew. Chem. 1930, **43**, 90: examination of an expressed Russian oil) find 17.8% and 20.5% of insoluble (fatty acid) hexabromides, respectively.

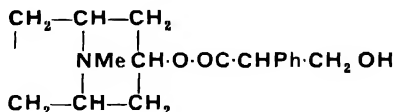
From 4.5 to 9.5% of saturated acids has been isolated from the oil by various observers, but the composition of the remaining unsaturated acids is uncertain. Kaufmann and Juschkevitch, using the thiocyanometric method, compute the composition of the fatty acids (iodine value 174.5) from an oil of iodine value 167 to be: saturated acids 10%,<sup>1</sup> oleic acid 12%, linoleic acid 53% and linolenic acid 25% (cf. Schestakoff and Kuptschinsky, Z. deut. Oel-u. Fett-Ind. 1922, **42**, 741). It is likely that the proportions of the unsaturated acids, and especially of linolenic acid, may vary with the climate of source or locality of the seed. Hempseed oil may be classed as a semi-drying oil, and is used, especially on the Continent, in the manufacture of green soft soap, and of boiled oils for the paint and varnish industry (cf. V. S. Kiselev and Charov, Maslob. Shir. Delo. 1929, No. 11, 24; Chim. et Ind. 1930, **23**, 1461; Kansas City Prod. Club, Oil, Paint and Drug Rep. 1935, **128**, No. 22, 64). In Asiatic countries the oil is extensively consumed as an edible oil, some 60-65% of the total Russian production being thus used [see report by Tilgner and Schillak, Polish Agric. and Forest Ann. 1938, **44**, No. 2/3, 437 (Amer. Chem. Abstr. 1938, **32**, 8613) on the suitability of refined hempseed oil for the

canning of fish] although the presence of traces of toxic or narcotic substances in the oil has occasionally been reported (cf. Kaufmann and Juschkevitch, l.c.; T. Y. Lo, Natl. Peiping Univ. Coll. Agric., Nutrit. Bull. B. 1935, (2), 22, 57). In the United States the use of hempseed oil in the paint industry is extending, and it has also been strongly recommended as a grinding oil for paint pigments (H. Friedman, Amer. Paint. J. 1936, **20**, January 13, 48). Its employment as a cosmetic oil has been suggested.

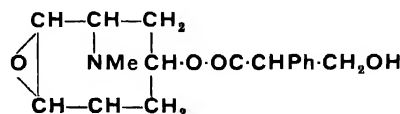
The expressed hempseed cake may be used in limited amounts as a feeding-stuff for cattle, although it is liable to contain traces of a narcotic principle (Lemcke, Seifens.-Ztg. 1907, **34**, 1229); in France and Belgium the cake is used as manure.

E. L.

**HENBANE**, *Hyoscyamus niger* Linn. (Solana-ceae), is a biennial herb, a native of Europe, North Africa and North and West Asia, and cultivated in England and elsewhere. The lower leaves vary in length up to 25 cm. and are ovate-lanceolate whilst the upper leaves are shorter, sessile and ovate-oblong; their margins are coarsely dentate and both surfaces are covered with long, soft hairs. The flowers, crowded together, arise in the axils of large, hairy bracts, are large, funnel-shaped and dull yellow with purple veinings. The fruit is a capsule. The seeds may be separated by sieving into two fractions according to size; the smaller produce annual plants whilst the larger give rise to biennials (Holmes, Pharm. J. 1921, **106**, 249). The whole plant emits a strong, characteristic odour and possesses a bitter, acrid taste. The dried leaves and flowering tops are official in the British Pharmacopœia, 1932, under the name of *Hyoscyamus* and are required to contain not less than 0.05% of the total alkaloids, calculated as *hyoscyamine*, and to comply with certain pharmacognostical standards. A liquid extract (0.045-0.055% total alkaloids), a dry extract (0.27-0.33% total alkaloids) and a tincture (0.0045-0.0055% total alkaloids) are the official preparations. Henbane contains the alkaloid *hyoscyamine*, the *lævo*-isomer of atropine (*tropyltropine*),



and smaller amounts of *hyoscyne*, the *l*-tropyl ester of scopine,



together with volatile bases similar to those in belladonna leaf. The roots contain a greater proportion of alkaloids than the aerial parts of the plant. Methods of estimation of the alkaloid content are described in the British (1932)

<sup>1</sup> I.e. 9.5% on the oil determined by Bertram's method.

and U.S.A. (XI) Pharmacopœias. (Critical reviews of available methods have been published by Caines and Evers (Pharm. J. 1926, 117, 179; Caines, Quart. J. Pharm. 1930, 3, 344), Exler (Pharm. Weekbl. 1928, 65, 1152), and Evans and Goodrich (J. Amer. Pharm. Assoc. 1933, 22, 824). For pharmacological methods of assay, see Nolle, Arch. exp. Path. Pharm. 1929, 143, 184; Jendrassik and Will, *ibid.* 1930, 153, 94; Fernandez, *ibid.* 1928, 127, 197, 204; Pulewka, *ibid.* 1932, 167, 96; Keil and Kluge, *ibid.* 1934, 174, 493; Trabucchi, Atti. Soc. med. chir. Padova, 1935, 13, 172.

W. H. L.

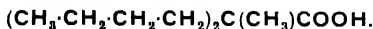
### HENDECOIC ACIDS (UNDECOIC ACIDS), $C_{11}H_{22}O_2$ .

(1) *n*-Undecylic Acid,  $CH_3[CH_2]_9COOH$ , is obtained by the reduction of undecylenic acid by hydrogen and colloidal palladium (Levene and West, J. Biol. Chem. 1914, 18, 464) or with hydrogen iodide and red phosphorus (Kraft, Ber. 1878, 11, 2219). Also by the oxidation of methylundecyl ketone with chromic acid (Kraft, *ibid.* 1929, 12, 1667). It may be obtained by heating  $\alpha$ -chloro- or  $\alpha$ -bromo-myristic acid to 350° with alkali, and by the oxidation of 6:7-dihydroxystearic acid with alkaline permanganate (Green and Hilditch, J.C.S. 1937, 764); m.p. 29–30°; b.p. 161°/15 mm., 179°/28 mm., 228°/160 mm.

*Amide*, m.p. 96–97°; 2-benzimidazole derivative, m.p. 114–114.5° (Pool, Harwood and Ralston, J. Amer. Chem. Soc. 1937, 59, 178). *Acid chloride*, b.p. 123°/11 mm. (Ford-Moore and Phillips, Rec. trav. chim. 1934, [iv], 53, 15, 847). Evidence for enantiotropism is given by the transition temperature 12.5–20° observed by Garner and Randall (J.C.S. 1924, 125, 887) and by the different heats of crystallisation of the two forms, and the X-ray examination (de Boer, Chem. Zentr. 1927, 1, 1410).

The zinc and magnesium salts find some use in cosmetics (*ibid.* 1934, 11, 1215; 1936, 11, 884). The triglyceride has also been prepared (Verkade, van der Lee and Meerburg, Rec. trav. chim. 1932, 51, 13). The ethyl ester condenses with benzene in the presence of aluminium chloride to give ethyl phenylundecylate and diethyl phenylundecylate (Baranger, F.P. 679041; Chem. Zentr. 1930, 11, 307).

#### (2) Methylidibutylacetic Acid,



Prepared by the oxidation of  $\alpha$ -methyl- $\alpha$ -dibutylacetone with 60% nitric acid (Meerwein, Annalen, 1919, 419, 148); b.p. 158–159°/18 mm. It is also obtained with other products in the oxidation of isobutylene. A white crystalline solid, m.p. 66–70°, soluble in alcohol and ether, insoluble in water.

(3) *Ethylpelargonic Acid*.—Prepared from 3-iodononane and sodiummalonic ester (Bagard, Bull. Soc. chim. 1907, [iv], 1, 359) or from  $\alpha$ -naphthylmalonic ester and ethyl bromide (Bowden and Adkins, J. Amer. Chem. Soc. 1934, 56, 689); b.p. 117–118°/5–6 mm.

(4) An acid,  $C_{11}H_{22}O_2$ , is obtained by blowing air through melted paraffin for some days at 130–135° (Bergmann, Z. angew. Chem. 1918, 31,

69); m.p. 53–7°, easily soluble in ether and light petroleum, but difficultly so in alcohol.

**HENDECENOIC ACID**,  $C_{11}H_{20}O_2$ , an acid obtained from alkaline extracts of petroleum distillates, b.p. 250–270° (Hell and Medinger, Ber. 1874, 7, 1217; 1877, 10, 451). It has also been termed *petroleumic acid*. Another hendecenoic acid is obtained by oxidising non-hydroxylated drying oils (U.S.P. 2020998). After sulphonation, or sulphonation of products of its condensation with aromatic hydrocarbons, it may be used as a substitute for Turkey Red oil.

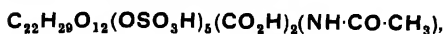
#### HENEQUEN (v. Vol. V, 166a).

**HENNA** (Al-henneh, Al-henna, or All-kenna). The dried leaf of a small shrub indigenous in Egypt and the Levant, also known as Egyptian privet, *Lawsonia alba*, *L. inermis* and certain other species of *L.* An aqueous infusion of the leaves has long been used in the East as a prophylactic against certain skin diseases; the root is alleged to be a specific against leprosy, the flowers yield a perfume and the fruit is used as an emmenagogue. The plant is cultivated mainly for the leaves; these are dried and powdered for use as the dyo henna, which as a stain for the hair, or for colouring the finger nails and soles of the feet, has been known from the earliest times. Lal and Dutt (J. Indian Chem. Soc. 1933, 10, 575) describe the uses of the plant in India for a diversity of ailments.

The colouring matter of henna has been investigated by Lal and Dutt (*l.c.*), by Tommasi (Gazzetta, 1920, 50, i, 263) and by Cox (Analyst, 1938, 63, 397). The leaves contain no tannin or starch but gallic acid and *lawsone*, which has been shown to be identical with 2-hydroxy-1:4-naphthoquinone, m.p. 192°; *acetyl* derivative, m.p. 128°, *monoxime*, m.p. 180°; 2:4-dinitrophenylhydrazine, m.p. 225°. *Lawson* is an acid dyestuff which dyes wool or silk a bright orange colour from an acid bath. Other colours can be obtained by use of a mordant (*cf.* Tommasi, *l.c.*). Air-dried henna leaves contain about 1–1.4% of 2-hydroxynaphthoquinone which may be determined quantitatively by reduction to trihydroxynaphthalene and titration in an atmosphere of carbon dioxide as described by Cox (*l.c.*). Processes have been patented for the extraction of *lawsone* from henna (B.P. 236557, 1924). For the composition of henna hair-dyes and compounded hennas, see HAIR DYES (HUMAN) (this Vol., p. 170c). See also ALKANET and ALKANNA.

**HEPAR SICC.** Liver extract, used in the treatment of *anæmia*; it produces a rise in the red blood cell count and relieves the symptoms. There are more than 50 proprietary preparations. The active principle against pernicious *anæmia*, "anahemin" (Dakin and West, J. Biol. Chem. 1935, 109, 489), appears to contain 2 substances (Wills *et al.*, Lancet, 1937, i, 311; Extra Pharmacopœia, 1941, 566). The Minister of Health (Pharm. J. 1941, i, 24, 71) has decided that liver extracts may not be administered to persons suffering from pernicious *anæmia* otherwise than by injection. This decision was extended to other megalocytic *anæmias* in "Liver Extract (Regulation of Use) Amendment Order, 1941."

**HEPARIN.** The anticoagulant substance prepared from liver and used in blood transfusion. A formula proposed is



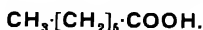
Extra Pharm. 1941, 575 (v. Vol. II, 23d, 24c).

**HEPTALDEHYDE**,  $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CHO}$ , also known commercially as *œnanthol*, b.p. 153–155°,  $d_{20}^{15.5}$  0.825,  $n_D^{20}$  1.415, is a synthetic perfume with a heavy, persistent fruity effect. It should never be used in greater amount in the finished product than 0.1% or it will destroy entirely the perfume value. It gives a very pleasant note to most floral bouquets.

E. J. P.

#### HEPTOIC ACIDS, $\text{C}_7\text{H}_{14}\text{O}_2$ .

(1) *n*-Heptoic Acid, *œnanthyl*ic Acid,



Formed by the oxidation of heptaldehyde (Organic Syntheses, 1936, 16, 39) and by the action of anhydrous potassium hydroxide at 220–230° on *n*-heptyl alcohol, the yield being nearly theoretical (Guerbet, Compt. rend. 1911, 153, 1489; Bull. Soc. chim. 1908, [iv], 2, 168). Also formed by the oxidation of castor oil and of oleic acid (Schorlemmer, Annalen, 1872, 161, 279; Tripier, Bull. Soc. chim. 1894, [iii], 11, 99).

An oily liquid, b.p. 222–224°; 118–119°/17 mm. Density 0.92217 (Bilterys and Gisseleire, Chem. Zentr. 1936, I, 3999). *Acid chloride*, b.p. 74–75°/1.9 mm. (Ford-Moore and Phillips, Rec. trav. chim. 1934, [iv], 53, 15). *Amide*, m.p. 94–95° (Asano, Chem. Zentr. 1922, I, 1227). It may be identified as its phenazine salt, m.p. 95–96° (Pollard, Adelson and Bam, J. Amer. Chem. Soc. 1934, 56, 1759); for its 2-benzimidazole, m.p. 137.5–138°, see Pool, Harwood and Ralston, J. Amer. Chem. Soc. 1937, 59, 178.

The acid is important in perfumery and an account of its preparation from castor oil has been published, "Das Ricinusöl als wichtiges Rohprodukt für die Darstellung synthetischer Riechstoffe," Riechstoffindustrie, 1927; see also Riv. ital. essenze profumi, 1930, 12, 58. The zinc and magnesium salts have been used in cosmetics (F.P. 45471, Pat. Add.).

(2) *iso*Heptoic Acid (*α*-methylhexoic acid),  $\text{CH}_3\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{COOH}$ .—Obtained by boiling hexyl cyanide with alcoholic potash (O. Hecht, Annalen, 1881, 209, 309) or by the reduction of fructose carboxylic acid (Kihani, Ber. 1885, 18, 3071). An oily, rancid-smelling liquid, b.p. 209.6°,  $d_{20}^{21}$  0.9138. Completely miscible with alcohol, ether, chloroform and carbon disulphide. Slightly soluble in water.

(3) *iso*Amylacetic Acid,



Prepared by the action of sodium and *iso*-amyl iodide upon ethyl acetate (Frankland and Duppa, Annalen, 1866, 138, 338) or by the distillation of *iso*amylmalonic acid (Paul and Hoffmann, Ber. 1890, 23, 1498), b.p. 216° (Levene and Allen, J. Biol. Chem. 1916, 27, 442),  $d_{20}^{19}$  0.9155 (Wallach, Annalen, 1915, 408, 190).

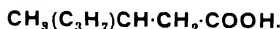
(4) Methyl-diethylacetic Acid (*αα*-methyl-ethylbutyric acid),  $\text{CMeEt}_2\cdot\text{COOH}$ .—Obtained by prolonged heating of methyl-diethyl-methyl cyanide with strong hydrochloric acid (E. Schdanoff, *ibid.* 1877, 185, 120), b.p. 207–208°/753 mm. Nearly insoluble in water.

(5) *β*-Methylcapronic Acid,



Prepared from malonic ester and *sec*-amyl alcohol (Dewael and Weckering, Bull. Soc. chim. Belg. 1924, 33, 495); b.p. 212–213°/755 mm. This acid is identical with the methylhexoic acid prepared by G. Ciamician and P. Silber (Atti. R. Accad. Lincei, 1908, [v], 17, 1, 185; Ber. 1908, 41, 1077; 1913, 46, 3080) from 1-methyl-hexan-3-one.

(6) Methyl*iso*propylpropionic Acid (*βγ*-dimethylvaleric acid),



Obtained by heating sodium *isovalerate* with sodium ethoxide in a stream of carbon monoxide (Geuther, Frolich and Looss, Annalen, 1880, 202, 321); b.p. 220°.

(7) Ethylpropylacetic Acid (*α*-ethylvaleric acid),  $\text{CHETPr}^a\cdot\text{COOH}$ .—Obtained by hydrolysing ethyl ethylpropylacetate with alkali (H. Kihani, Ber. 1886, 19, 227), b.p. 209–2°.

The acid and its salts have been used as vulcanisation regulators (U.S.P. 1997700).  
(8) Ethyl*iso*propylacetic Acid (*αγ*-dimethylvaleric acid),  $\text{CHETPr}^b\cdot\text{COOH}$ .—It has been reported (G.P. 441272; Chem. Zentr. 1927, I, 2137) to have been obtained from methyl alcohol, carbon monoxide and hydrogen, by heating under pressure and treating the resulting oil with alkali. It may be prepared by the standard malonic ester synthesis (M. W. Burrows and W. H. Bentley, J.C.S. 1895, 67, 511); b.p. 204–205°.

**HEPTYL ALCOHOL.** This alcohol,  $\text{C}_7\text{H}_{14}\text{O}$ , and its esters are sometimes used in perfumery, and the series of esters from the formate to the valerianate have been prepared and put on the market. Their value in synthetic perfumery is mostly of a "text-book" nature, and they are not of any real importance to the perfume industry.

E. J. P.

#### *n*-HEPTYLSUCCINIC ACID,



Formed by the reduction of *n*-hexyl-itaconic, -citraconic or -mesaconic acid with sodium amalgam (Fittig and Hoeffken, Annalen, 1899, 304, 337); m.p. 90–91°. Soluble in water and chloroform, difficultly soluble in benzene.

"HERATOL" (v. Vol. I, 75a).

"HEROIN." Acetomorphine. Diacetylmorphine, used as a sedative.

**HERBACETIN, HERBACITRIN** (v. Vol. III, 407a).

**HERCYNITE** (v. Vol. IV, 279d).

**HERDERITE** (v. Vol. I, 685a).

"HERMITE FLUID," (v. Vol. IV, 20d).

**HERRING OIL** (v. Vol. V, 228d).

"HERTOLAN" (v. Vol. II, 264c).

**HERZENBERGITE.** Tin sulphide,  $\text{SnS}$ , as black, flaky orthorhombic crystals, closely resembling *francite* (*q.v.*) and *teallite* (and to some extent also *graphite*) in appearance. As a natural mineral it was first recognised from the Maria Teresa mine, Huari, Bolivia, by R. Herzenberg in 1932 and named by him *kolbeckine*. This name being preoccupied, it was later renamed *herzenbergite* and proved to be identical with artificial  $\text{SnS}$ . The mineral has also been found in small amount in the Stiepelmann mine near Arandis in South-West Africa (P. Ramdohr, Z. Krist. 1935, **92**, 186; W. Hofmann, *ibid.* 1935, **92**, 161). Crystals of the same kind are formed during tin smelting when the ore contains sulphides. These were at first described as an orthorhombic modification of tin (" $\beta$ -tin"), but afterwards proved to be  $\text{SnS}$  (L. J. Spencer, Min. Mag. 1921, **19**, 113).

L. J. S.

**HESPERITIC ACID** (*n. Vol. V*, 61a).

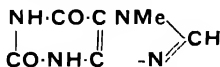
**HESSITE or TELLURIC SILVER.**

Silver telluride,  $\text{Ag}_2\text{Te}$ , crystallised in the cubic system and isomorphous with *argentite* (*q.v.*). The silver ( $\text{Ag}$  63.3%) is often partly replaced isomorphously by gold, forming a passage to *petzite*. The colour is lead-grey, and the material somewhat sectile; sp.gr. 8.3–8.9, hardness 2½–3. The best crystals, though much distorted, are from Botes in Transylvania, and massive material was formerly obtained in some quantity in the Slavodinsk mine in the Altai Mountains, Siberia. The mineral has also been found in California, Colorado and Utah.

L. J. S.

**HESSONITE** *v.* GARNET.

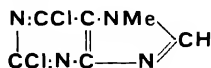
**HETEROXANTHINE**, 7-methylxanthine, 2:6-dioxy-7-methylpurine,



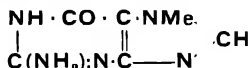
occurs together with xanthine and paraxanthine as a constituent of normal human urine (Salomon, Ber. 1885, **18**, 3406; Virchow's Archiv. 1891, **125**, 554; Wada, Acta Schol. Med. Univ. Imp. Kyoto, 1930, **13**, 187); 10,000 litres yielded 22.2 g. of the mixed bases, of which 11.36 g. was heteroxanthine (Salomon and Krüger, Z. physiol. Chem. 1898, **24**, 364); it occurs also with xanthine in the urine of the dog (Salomon, *ibid.* 1887, **11**, 410). Heteroxanthine appears to be a product of the metabolism of theobromine and caffeine, for when these alkaloids are administered to rabbits, dogs or men, heteroxanthine appears in the urine (Bořdzynski and Gottlieb, Ber. 1895, **28**, 1113). According to Albanese (Gazzetta, 1895, **25**, ii, 298) heteroxanthine is an intermediate product in the degradation that caffeine undergoes in the organism, the methyl groups being successively removed until xanthine is obtained, which is then converted into urea and ammonia. Heteroxanthine acts as a powerful diuretic on dogs and rabbits when injected hypodermically in small doses; larger doses are toxic, an injection of 1 g. killed a dog weighing 8 kg. in 10 days (Albanese, *l.c.*; cf. Krüger and Salomon, Z. physiol. Chem. 1895, **21**, 169; Schmiedeberg, Ber. 1901, **34**, 2556).

The isolation of heteroxanthine from yeast (1.2 g. from 40 kg. dried brewer's yeast) has been described by Wiardi and Jansen (Rec. trav. chim. 1934, **53**, 205). The yeast was extracted with water containing 0.1% benzoic acid. The bases were adsorbed on fuller's earth, extracted with barium hydroxide solution, precipitated with sodium silicotungstate and then purified by precipitating twice with silver nitrate in  $N/100 \text{ HNO}_3$ . The heteroxanthine was recrystallised from  $N/2$  hydrochloric acid.

The synthesis of heteroxanthine from theobromine (*n. Vol. II*, 197c) has been effected by Fischer (Ber. 1897, **30**, 2400). When 2:6-dichloro-7-methylpurine,



obtained by the action of phosphoryl chloride on theobromine, is heated at 120–125° with hydrochloric acid (sp. gr. 1.19), it is converted into the hydrochloride of heteroxanthine. When 2:6-dichloro-7-methylpurine is heated with allyl alcohol and sodium, it yields 2:6-dialloxy-7-methylpurine, m.p. 111–112°, which may be reduced catalytically to heteroxanthine (Bergmann and Heimhold, J.C.S. 1935, 1365). Another synthesis was carried out by Sarasin und Wegmann (Helv. Chim. Acta, 1924, **7**, 713); the nitrate of 5-chloro-1-methylglyoxaline, when treated with concentrated sulphuric acid, is converted to 5-chloro-4-nitro-1-methylglyoxaline, m.p. 147–148°, which, on heating with potassium cyanide and a little iodide in alcoholic solution, gives 4-nitro-5-cyano-1-methylglyoxaline, m.p. 141–142°. Hydrolysis of this nitrile gives the amide, m.p. 257–258° (decomp.), and then reduction yields the amide of 4-amino-1-methylglyoxalincarcboxylic acid (m.p. 184–185°, hydrochloride, m.p. 214–215°). This amino-amide reacts with ethyl carbonate at 160–170° to give heteroxanthine. Krüger and Salomon (Z. physiol. Chem. 1898, **26**, 389) also obtained it by the action of nitrous acid on epiguanine (7-methylguanine, 2-amino-6-oxy-7-methylpurine),



and as Fischer (*l.c.*) has synthesised epiguanine, this method is also synthetic.

Heteroxanthine is a crystalline powder; when heated gradually it melts and decomposes at 341–342°, when heated rapidly it darkens at 360° and melts and decomposes at 380°. It dissolves in 142 parts of boiling water (Fischer, *l.c.*) or in 7,575 parts of alcohol at 17°, or in 2,250 parts at the boiling-point (Bořdzynski and Gottlieb, Ber. 1895, **28**, 1113). Heteroxanthine possesses both acidic and basic properties, the basic ( $k_b$ ) and acidic ( $k_a$ ) dissociation constants being  $11.82 \times 10^{-14}$  and  $4.019 \times 10^{-11}$  respectively (Wood, J.C.S. 1906, **89**, 1840). For the dissociation constants in water and 90% alcohol at 18°, see Ogston (J.C.S. 1935, 1376); and for the ultra-violet absorption spectrum, see Guland and Holiday (Nature, 1933, **132**, 782) and

(Gulland, Holiday and Macrae (J.C.S. 1934, 1639).

Heteroxanthine forms salts with acids which are readily dissociated in water; the *hydrochloride* crystallises in tufts of transparent crystals, and yields a micro-crystalline *platini-chloride*; the *sulphate*,  $C_6H_5O_2N_4 \cdot H_2SO_4$ , is decomposed by water. Heteroxanthine forms a characteristic *sodium* derivative,



crystallising in plates or prisms, melting at about  $300^\circ$ , readily soluble in water, sparingly so in sodium hydroxide; the *potassium* derivative has similar properties and a higher melting-point (Salomon, Ber. 1885, 18, 3406; Virchow's Archiv. 1891, 125, 554). Heteroxanthine yields a crystalline precipitate with mercuric chloride, and forms a crystalline derivative with silver nitrate. It is also precipitated by copper acetate, phosphotungstic acid or lead acetate in the presence of ammonia (Salomon, *loc. cit.*). It is differentiated from hypoxanthine, xanthine and guanine by the sparing solubility of its sodium derivative in sodium hydroxide; it differs from paraxanthine in its solubility and in not yielding a precipitate with picric acid in the presence of hydrochloric acid.

When a solution of heteroxanthine containing chlorine-water and nitric acid is evaporated, the residue develops a red colour with ammonia, becoming blue on addition of sodium hydroxide. On oxidation with potassium permanganate in concentrated sulphuric acid, heteroxanthine yields three of its four nitrogen atoms as ammonia or urea, and the fourth as methylamine (Jolles, Ber. 1900, 33, 2120, 2126).

By electrolytic reduction in sulphuric acid solution, heteroxanthine yields 2-oxy-7-methyl-1,6-dihydropurine (Tafel and Weinschenk, *ibid.* 1900, 33, 3374).

### HETEROGENEOUS REACTIONS.

Heterogeneous reactions, by definition, take place at phase boundaries or involve transport of matter across the boundaries. The possible phase boundaries are:

gas-solid; liquid-solid; gas-liquid;  
liquid-liquid; solid-solid.

Reactions at each of these phase boundaries will be briefly reviewed in turn. The phenomena covered by the term "heterogeneous reaction" include many processes discussed elsewhere in this dictionary (*v. DIFFUSION*, Vol. III, 604*b*; *CRYSTALLISATION*, Vol. III, 445*d*; *CATALYSIS IN INDUSTRIAL CHEMISTRY*, Vol. II, 422*d*; *HARDENED OR HYDROGENATED OILS*, this Vol., p. 177*b*; *ABSORPTION*, Vol. I, 66; and *ADSORPTION*, Vol. I, 147*d*). The present article will therefore describe the underlying principles and modern examples of certain processes, but for reasons of space will deal primarily with reactions usually regarded as chemical.

#### A. REACTIONS AT THE GAS-SOLID INTERFACE.

(i) **Systematic Classification of the Kinetics of Heterogeneous Reactions.**—A reaction at an interface may be controlled by any one of the steps:

- (a) Transport of reactants to the interface.
- (b) Adsorption of the gases.
- (c) Reaction on the surface.
- (d) Desorption of the products.
- (e) Transport of the liberated products away from the surface.

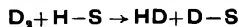
(a) and (e) are normally diffusion processes. (b) and (d) may be chemical or physical in nature, while (c) is the essentially chemical process. In the majority of reactions at gas-solid interfaces (c) governs the reaction velocity. First, however, the less usual steps will be considered.

*Diffusion as a Rate-Determining Step.*—Diffusion is of primary importance in many reactions at liquid-solid interfaces (p. 215*b*). It may also control reaction rates at the gas-solid interface when the solid is present as a porous mass. Diffusion to and from the important internal surfaces is then slow enough to govern the rate of reaction. This has been observed during coal or coke combustion under special conditions (Tu, Davis and Hottel, Ind. Eng. Chem. 1934, 26, 749; see also p. 215*a*) and in the activated adsorption of hydrogen by charcoal at high temperatures (Barrer, Proc. Roy. Soc. 1935, A, 149, 256). As a rule, however, it is a supernumerary phenomenon in heterogeneous gas reactions.

*Sorption and Desorption as Rate-Determining Steps.*—At high temperatures on certain surfaces, for example, charcoal, the ortho-para conversion of hydrogen may occur by activated adsorption of hydrogen (p. 214*b, d*), followed by desorption (A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, 1935, p. 89).



The overall reaction rate is controlled in this case by the sorption and desorption velocities. The same mechanism has been proposed for exchange reactions between hydrogen and deuterium. An alternative suggestion, however, is that the ortho-para hydrogen conversion occurs by exchange between gaseous molecules or molecules sorbed by Van der Waals forces and the chemisorbed layer:



where S denotes an atom of the surface.

Desorption of nitrogen is probably rate-controlling in the decomposition of  $NH_3$  by iron (Taylor and Jungers, J. Amer. Chem. Soc. 1935, 57, 660); and chemisorption of nitrogen by iron may be the slowest process in the technically important synthesis of ammonia using iron catalysts. Hinshelwood ("Kinetics of Chemical Change," Oxford University Press, 1940, p. 207) then gives as a general reaction equation:

$$\text{Rate} = k_2\theta[B] = \frac{k_1k_2[A][B]}{k_1[A] + k_2[B]} \quad (1)$$

where A is the reactant undergoing slow adsorption ( $N_2$ ) with a velocity constant  $k_1$ . A is

removed by reaction with B ( $H_2$ ), the velocity constant for this process being  $k_2$ .  $\theta$  denotes the fraction of the total available surface covered by A. If, as in ammonia synthesis,  $k_1 \ll k_2$  the rate equation reduces to

$$\text{Rate} = k_1[A] \quad (2)$$

*Chemical Reaction as a Rate-Determining Step.*  
—The number of adsorbed atoms or molecules of reactants and resultants controls the reaction rate and thus quantitative aspects of adsorption equilibrium must be reviewed.

Langmuir (J. Amer. Chem. Soc. 1916, **38**, 2268) deduced a simple isotherm for an immobile monolayer by equating the velocities of adsorption and desorption at equilibrium :

$$\text{Velocity of adsorption} = k_1 p(1-\theta) \quad (3)$$

$$\text{Velocity of desorption} = k_2 \theta \quad (4)$$

whence

$$a = \frac{ap}{1+ap} \quad (5)$$

where  $k_1$ ,  $k_2$  are constants, and  $a = \frac{k_1}{k_2}$ ; and where

TABLE I.—UNIMOLECULAR PROCESSES.

No	Conditions.	Rate equation.	Examples.
1.	Single reactant weakly adsorbed.	$-\frac{dx}{dt} = k\theta = kap$	$N_2O$ on gold. <sup>1</sup> $HI$ on Pt. <sup>2</sup> $PH_3$ on porcelain <sup>3</sup> and glass <sup>4</sup> . $H_2Se$ on Se. <sup>5</sup> $AsH_3$ on glass. <sup>6</sup> $H-CO_2H$ vapour on glass, Pt, Rh, $TiO_2$ . <sup>7</sup>
2.	Single reactant moderately adsorbed.	$-\frac{dx}{dt} = k\theta = \frac{kap}{1+ap}$ $\approx kp^n$ ( $n$ denotes an exponent less than one.)	$SbH_3$ on Sb. <sup>8, 9</sup>
3.	Single reactant strongly adsorbed.	$-\frac{dx}{dt} = k\theta = \lambda \frac{a}{b}$	$HI$ on gold. <sup>10</sup> $NH_3$ on W (at moderate or low temperatures). <sup>11</sup> $NH_3$ on Mo and Os. <sup>12</sup>
4.	Single reactant weakly adsorbed, resultant moderately adsorbed.	$-\frac{dx}{dt} = k\theta = \frac{kap_1}{1+bp_2}$	$N_2O$ on Pt (retarded by $O_2$ ). <sup>13</sup>
5.	Single reactant weakly adsorbed, resultant strongly adsorbed.	$-\frac{dx}{dt} = k\theta = \frac{kap_1}{bp_2}$	$NH_3$ on Pt wire at $1,000^\circ C$ . <sup>14</sup> (retarded by $H_2$ ).
6.	Reactant and resultant both strongly adsorbed.	$-\frac{dx}{dt} = k\theta = \frac{kap_1}{ap_1 + bp_2}$	Dehydrogenation of alcohol in presence of $H_2O$ , $CH_3CO-CH_3$ or benzene, as increasingly effective poisons. <sup>15</sup>
7.	Single reactant weakly adsorbed, two resultants strongly adsorbed.	$-\frac{dx}{dt} = k\theta = \frac{kap_1}{bp_2 + ap_3}$	$NH_3$ on Pt in pressure range $0-0.1$ mm. (Retardation by $N_2$ and $H_2$ ). <sup>16</sup>

Hinshelwood and Prichard, Proc. Roy. Soc. 1925, A, **108**, 211.

Hinshelwood and Burk, J.C.S. 1925, **127**, 2896.

Trautz and Bhandarkar, Z. anorg. Chem. 1919, **106**, 95.

Hinshelwood and Topley, J.C.S. 1924, **125**, 393.

Bodenstein, Z. physikal. Chem. 1899, **29**, 429.

Van't Hoff, "Etudes de dynamique chimique," Amsterdam, 1884, p. 83.

Hinshelwood and Topley, J.C.S. 1923, **123**, 1014.

Hinshelwood, *op. cit.* p. 191.

Stock and Bodenstein, Ber. 1907, **40**, 570; Stock, Gomolka and Heynemann, *ibid.*, p. 532.

Hinshelwood and Prichard, J.C.S. 1925, **127**, 1552.

Hinshelwood and Burk, J.C.S. 1925, **127**, 1105.

Burk, Proc. Nat. Acad. Sci. 1927, **13**, 87; Kunsman, J. Amer. Chem. Soc. 1928, **50**, 2100; Arnold and Burk,

J. Amer. Chem. Soc. 1932, **54**, 23.

Hinshelwood and Prichard, J.C.S., 1925, **127**, 327.

Hinshelwood and Burk, J.C.S. 1925, **127**, 1114; Schwab and Schmidt, Z. physikal. Chem. 1929, B, **3**, 337.

Constable, Proc. Camb. Phil. Soc. 1926, **23**, 176, 593.

Schwab and Schmidt, Z. physikal. Chem. 1929, B, **3**, 337.



TABLE II.—BIMOLECULAR PROCESSES.

No.	Conditions.	Rate equation.	Examples.
1.	Two reactants weakly adsorbed.	$\frac{dx}{dt} = k\theta_1\theta_2$ $= k(ap_1)(bp_2)$	H <sub>2</sub> and C <sub>2</sub> H <sub>4</sub> on weakly active Cu. <sup>1</sup> C <sub>2</sub> H <sub>4</sub> and Br <sub>2</sub> on glass. <sup>2</sup>
2.	Two reactants, one weakly, one moderately adsorbed.	$\frac{dx}{dt} = k\theta_1\theta_2$ $= k \frac{(ap_1)(bp_2)}{(1+bp_2)}$	Water gas reaction H <sub>2</sub> +CO <sub>2</sub> →CO+H <sub>2</sub> O at 1,000°C. on Pt (retardation by CO <sub>2</sub> ). <sup>3</sup>
3.	Two reactants, one weakly, one strongly adsorbed.	$\frac{dx}{dt} = k\theta_1\theta_2$ $= k \frac{ap_1}{bp_2}$	Oxidation of H <sub>2</sub> on Pt below 700°C. (retardation by H <sub>2</sub> ). <sup>4</sup> Oxidation of CO on Pt below 700°C. (retardation by CO). Oxidation of CO on quartz, <sup>5</sup> H <sub>2</sub> and C <sub>2</sub> H <sub>4</sub> on active Cu between 0°C and 20°C. <sup>6</sup>
4.	Two reactants, but only one kinetically active.	$\frac{dx}{dt} = k\theta_1\theta_2$ $= kp_1 \text{ or } kp_2$ <p>according as the pressure of 1 or 2 is much the greater.</p>	Reaction of CO and O <sub>2</sub> on Pt above 700°C. Surface probably saturated with component in excess. Reaction occurs when the other component bombards this surface. <sup>4</sup>
5.	Two reactants, one product strongly sorbed.	$\frac{dx}{dt} = k\theta_1\theta_2$ $= \frac{k(ap_1)(bp_2)}{cp_3}$ $\frac{dx}{dt} = k\theta^2$ $= \frac{k(ap_1)^2}{cp_3}$ <p>when 1 and 2 are of the same kind.</p>	Decomposition of NO on Pt-Rh (retardation by O <sub>2</sub> ). <sup>7</sup>
6.	Two reactants, one strongly sorbed, and the other moderately sorbed on remaining part of the surface.	$\frac{dx}{dt} = k\theta_1\theta_2$ $= \frac{k(ap_1)}{(1+bp_2)}$ $\sim \frac{k(ap_1)}{(bp_2)^n}$ <p>(n&lt;1)</p>	Oxidation of SO <sub>2</sub> to SO <sub>3</sub> on Pt. O <sub>2</sub> is strongly sorbed and SO <sub>3</sub> retards the reaction. <sup>8</sup>

<sup>1</sup> Pease, J. Amer. Chem. Soc. 1923, **45**, 1196; Grassi, Nuovo Cim. 1916, [vi], **11**, 147.<sup>2</sup> Stewart and Edlund, J. Amer. Chem. Soc. 1923, **45**, 1014.<sup>3</sup> Hinshelwood and Prichard, J.C.S. 1925, **127**, 800.<sup>4</sup> Langmuir, Trans. Faraday Soc. 1922, **17**, 621.<sup>5</sup> Bouenstein and Ohlmer, Z. physikal. Chem. 1905, **53**, 166.<sup>6</sup> Pease, l.c.<sup>7</sup> Bachman and G. B. Taylor, J. Physical Chem. 1929, **33**, 447.<sup>8</sup> Bodenstein and Fink, Z. physikal. Chem. 1907, **60**, 1.

$\theta$  denotes the fraction of the whole surface covered by the monolayer. This simple isotherm expresses well the  $\theta$ - $p$  relations of many sorption systems (see, however, p. 211b). The isotherm was deduced for a homogeneous surface and many of the deviations from it are due to the presence of capillaries and cracks in the surface, and to the presence of other adsorbed impurities. The isotherm was originally deduced for an immobile monolayer but equations of similar form are obtained for mobile monolayers (Volmer, Z. physikal. Chem. 1925, **115**, 253) and the adsorption isotherm may be accurately determined using statistical mechanics (Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1939, pp. 426 *et seq.*).

The Langmuir isotherm is thus a convenient

basis for the classification of heterogeneous processes. For example, a unimolecular reaction may occur in an adsorbed film. Then, at low pressures :

$$-\frac{dx}{dt} = k\theta - kap$$

since  $\theta = \frac{ap}{1+ap}$  and for small  $p$ ,  $ap \ll 1$ .

At intermediate pressures  $-\frac{dx}{dt} = k\theta = \frac{kap}{1+ap}$

while at high pressures

$$-\frac{dx}{dt} = k, \text{ since for large } p, ap \gg 1.$$

When two gases exerting equilibrium pressures  $p_1$  and  $p_2$  respectively are simultaneously adsorbed, the isotherms may be expressed by

$$\theta_1 = \frac{ap_1}{1+ap_1+bp_2} \quad (6)$$

$$\theta_2 = \frac{bp_2}{1+ap_1+bp_2} \quad (7)$$

where  $\theta_1, \theta_2$  are the fractions of the surface covered by each component and  $a$  and  $b$  are constants. One of these gases may be a reactant, one a resultant, or both may be reactants. Similar isotherms obtain when more than two gases are competing for the surface. Should the resultant cover the whole surface the reactant is almost completely displaced and the resultant then poisons or retards the reaction. If the subscript 2 refers to this resultant

$$bp_2 \gg ap_1 \text{ or } 1 \text{ and so } \theta_1 = \frac{ap_1}{bp_2}$$

Thus in a unimolecular process

$$-\frac{dx}{dt} = k\theta_1 = \frac{kap_1}{bp_2}$$

Many such possibilities can arise and a systematic classification of heterogeneous reactions in terms of Langmuir's isotherm has been made. In Tables I and II are summarised different reaction equations, the conditions giving rise to them and examples of heterogeneous processes obeying them. Reactions of a higher order than bimolecular are rare but are amenable to the treatments of Tables I and II.

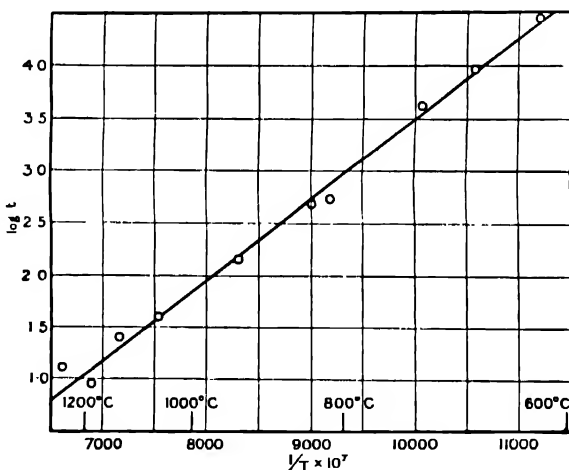


FIG. 1. INFLUENCE OF TEMPERATURE UPON THE HETEROGENEOUS DECOMPOSITION OF  $N_2O$  ON A PLATINUM WIRE.  $t$  is the Time Required for Half Decomposition ( $t \propto \frac{1}{k}$ ).

(ii) **The Order of Heterogeneous Reactions.**—The data of Tables I and II show that the real order of a heterogeneous reaction may have little or no relation to the form of the equation governing the kinetics. The latter are controlled by adsorption equilibria. The apparent order and the true order of a reaction are the same only when the amount of each reactant adsorbed is proportional to its equilibrium pressure.

(iii) **The Activation Energy of Heterogeneous Reactions.**—The velocity constant  $k$  of a heterogeneous reaction usually obeys the equation

$$\ln k = -\frac{E_a}{RT} + \text{constant} \quad (8)$$

where  $k$  is the velocity constant, and  $E_a$  denotes the apparent energy of activation. This is illustrated in Fig. 1 for a typical instance.

The adsorption equilibria, however, alter with temperature, and therefore the term  $E_a$  may include the heat of adsorption,  $\Delta H$ , or a function of  $\Delta H$ , for each reactant and resultant, according to an expression analogous to the Clapeyron equation.<sup>1</sup>

<sup>1</sup> This expression takes the form

$$\left( \frac{\delta \ln \theta}{\delta T} \right)_p = -\frac{\Delta H}{RT^2}$$

where  $\theta$  denotes the fraction of the surface covered at constant pressure  $p$ , and  $\Delta H$  is the heat of adsorption.

Simple examples have been worked out (H. S. Taylor, "Treatise on Physical Chemistry," Macmillan & Co., 2nd ed., 1931, Vol. II, pp. 1081 *et seq.*) and the relations between the true and apparent activation energies  $E_t$  and  $E_a$ , respectively, are summarised below.

**Surface Saturated with Reactant at Both Temperatures.**—The reaction is of apparent zero order at both temperatures; the surface population of reactant molecules does not alter and the heat of adsorption is not involved in  $E_a$ . Therefore

$$E_t = E_a.$$

*E.g.* decomposition of HI on Au (Table I, ref. 10)  $E_a = E_t = 25,000$  g.-cal. per g.-mol.; decomposition of  $\text{NH}_3$  on W (Table I, ref. 11)  $E_a = E_t = 42,000$  g.-cal. per g.-mol.

**Process Unimolecular and Reactant Weakly Adsorbed.**—The surface population decreases with increasing temperature if sorption occurs exothermically and  $E_a = E_t + \Delta H_1$ . Here  $\Delta H_1$  denotes the heat of adsorption and following thermodynamic convention is to be given a negative sign for an exothermal sorption. If  $\Delta H_1$  is appreciable,  $E_a$  may be small. *E.g.* decomposition of HI on Pt wire (Table I, ref. 2)  $E_a = 14,000$  g.-cal. per g.-mol.

**Process Unimolecular, Reactant Weakly Adsorbed and Resultant Strongly Adsorbed.**—In this case  $E_a = E_t + \Delta H_1 - \Delta H_2$  where the subscript 1 refers to reactant and 2 to resultant. When the resultant is strongly adsorbed,  $\Delta H_2$  is large and therefore  $E_a$  may become very great. *E.g.* decomposition of  $\text{NH}_3$  on Pt (Table I, ref. 14)  $E_a \approx 140,000$  g.-cal. per g.-mol. The reaction is inhibited by hydrogen and  $\Delta H_2$  for the adsorption of hydrogen on platinum may be as large as  $-100,000$  g.-cal. per g.-mol.

**Bimolecular Process with Two Reactants Weakly Adsorbed.**—Then  $E_a = E_t + \Delta H_1 + \Delta H_2$  where the subscripts refer now to the two reactants. *E.g.*  $\text{C}_2\text{H}_4 + \text{H}_2 \xrightarrow{\text{Cu}} \text{C}_2\text{H}_6$  (Table II, ref. 1). The copper must be weakly active and the temperature above  $200^\circ\text{C}$ . Then  $E_a \approx 10,000$  g.-cal. per g.-mol.

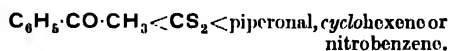
**Bimolecular Process, One Reactant Weakly and one Strongly Adsorbed.**—The relation now is  $E_a = E_t + \Delta H_1 - \Delta H_2$  where the subscript 2 refers to the strongly adsorbed reactant,

*e.g.*  $\text{C}_2\text{H}_4 + \text{H}_2 \xrightarrow{\text{Cu}} \text{C}_2\text{H}_6$  (Table II, ref. 6). The reaction is now confined to low temperatures on active copper. Since  $E_a$ ,  $\Delta H_1$  and  $\Delta H_2$  under these conditions are 10,000,  $-11,000$  and  $-16,000$  g.-cal. per g.-mol. respectively,  $E_t$  must be  $\approx 5,000$  g.-cal. per g.-mol.

(iv) **Inhomogeneity of surfaces.**—Inhomogeneity of surfaces may show itself in several ways. Thus it may modify the adsorption isotherms until the Langmuir treatment of adsorption no longer applies and the heat of sorption varies with  $\theta$ , the fraction of the surface covered (*e.g.* Barrer, Proc. Roy. Soc. 1937, A, 161, 476; Garner and Kingman, Trans. Faraday Soc. 1931, 27, 322). The true activation energy may also vary with  $\theta$  (Barrer, Proc. Roy. Soc. 1935, A, 149, 253; J.C.S. 1936, 1256) and,

furthermore, there may be areas of the surface upon which one reaction occurs and other areas where a second reaction takes place, both reactions involving the same reactants (Taylor, Proc. Roy. Soc. 1925, A, 108, 105; Hinshelwood, *op. cit.* p. 225).

This last phenomenon may be considered further. Frequently the effect of a surface in promoting a reaction is destroyed by minute traces of some poison (*cf.* Table VIII). The active fraction of a surface may thus be very small. Moreover, catalysts may be poisoned with respect to one reaction while remaining active in promoting others. Carbon disulphide in suitable amount inhibits the hydrogenation of  $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_3$  but does not prevent reduction of cyclohexene, piperonal and nitrobenzene, all on the surface of platinum black (Vavon and Hussen, Compt. rend. 1922, 175, 277). Perhaps these results are to be explained in terms of selective sorption in which the affinity for the platinum increases in the order:



Other examples of this behaviour have been instanced by Hinshelwood (*op. cit.* p. 227) and by Yoshikawa (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1042).

Another view, the adlineation theory of active centres, is due to Schwab and Pietsch (Z. physikal. Chem. 1928, B, 1, 385; *ibid.* 1929, B, 2, 262; Z. Elektrochem. 1929, 35, 573; Schwab, "Die Katalyse, vom Standpunkt der chemischen Kinetik," J. Springer, Berlin, 1931); according to this theory the centres are crystal grain boundaries. Reaction would then occur primarily along a network of lines intersecting the surface of any natural crystal and following the grain boundaries.

Considerable evidence has been accumulated by Maxted and co-workers (Maxted and Lewis, J.C.S. 1933, 502; Maxted and Stone, *ibid.* 1934, 26, 672; Maxted and Moon, *ibid.* 1935, 393, 1190; 1936, 635) which appears to contradict the concept of active centres. These data indicate the catalyst surface to be energetically homogeneous for certain reactions, such as the decomposition of  $\text{H}_2\text{O}_2$  by platinum.

The inhomogeneity of surfaces leads to kinetic consequences of interest. Some reactions have to be interpreted as though there were a multiple adsorbing surface on different zones of which the reactants are independently adsorbed. The kinetics in Table III have been analysed from this standpoint, although certain of the mechanisms are open to alternative interpretations (*e.g.* No. 2, Table III, and No. 4, Table II). On the present view, in order to have a reaction, the independent adsorbing sites must be mixed up among one another so that the reactants are in juxtaposition, or else surface diffusion must be possible with reaction at the boundaries of the two-dimensional phases.

(v) **Comparison between Homogeneous and Heterogeneous Reactions.**—Certain reactions occur by both homogeneous and heterogeneous mechanisms. Instances where the true energies of activation have been determined for

TABLE III.—TWO SURFACES—BIMOLECULAR REACTIONS.

No.	Conditions.	Sorption isotherms.	Kinetics.	Examples.
1.	Reactant 1 weakly, reactant 2 moderately adsorbed, each independently of the other.	$\theta_1 = ap_1$ on surface 1. $\theta_2 = \frac{bp_2}{1+bp_2}$ on surface 2.	$-\frac{dx}{dt} = k\theta_1\theta_2$ $= \frac{k(ap_1)(bp_2)}{1+bp_2}$	Oxidation of CO on quartz. Oxygen is weakly adsorbed. <sup>1</sup>
2.	Reactant 1 weakly, reactant 2 strongly adsorbed, each independently of the other.	$\theta_1 = ap_1$ on surface 1. $\theta_2 = 1$ on surface 2.	$-\frac{dx}{dt} = k_1\theta_1\theta_2$ $= k_1(ap_1)$	Oxidation of CO on porcelain, Au, Ni, Cu, NiO, CuO. <sup>2</sup>
3.	Reactants 1 and 2 strongly and independently adsorbed.	$\theta_1 = 1$ on surface 1. $\theta_2 = 1$ on surface 2.	$-\frac{dx}{dt} = k\theta_1\theta_2$ $= k$	$H_2 + C_2H_4 = C_2H_6$ on Ca + CaH <sub>2</sub> . <sup>3</sup>
4.	Reactants 1 and 2 moderately and independently adsorbed.	$\theta_1 = \frac{ap_1}{1+ap_1}$ on surface 1. $\theta_2 = \frac{bp_2}{1+bp_2}$ on surface 2.	$-\frac{dx}{dt} = k\theta_1\theta_2$ $= \frac{k(ap_1)(bp_2)}{(1+ap_1)(1+bp_2)}$ $\simeq k(ap_1)^m(bp_2)^n$ where $n, m < 1$ .	$H_2 + CO_2 = CO + H_2O$ on W. <sup>4</sup> $H_2 + N_2O = N_2 + H_2O$ on Au. <sup>5</sup> $2H_2 + O_2 = 2H_2O$ on porcelain. <sup>6</sup>

<sup>1</sup> Benton and Williams, J. Physical Chem. 1926, **30**, 1487.<sup>2</sup> Bone and Andrew, Proc. Roy. Soc. 1925, A, **109**, 459; *ibid.* 1926, A, **110**, 16; Bone and Forshaw, Proc. Roy. Soc. 1927, A, **114**, 160.<sup>3</sup> Pease and Stewart, J. Amer. Chem. Soc. 1925, **47**, 2763.<sup>4</sup> Hinshelwood and Prichard, J.C.S. 1925, **127**, 1546.<sup>5</sup> Hinshelwood and Hutchinson, J.C.S. 1926, **129**, 1556.<sup>6</sup> Bodenstein, Z. physikal. Chem. 1899, **29**, 665.

both mechanisms are given in Table IV. These data show that the homogeneous process takes

TABLE IV.—COMPARISON OF ENERGIES OF ACTIVATION FOR HOMOGENEOUS AND HETEROGENEOUS REACTIONS.<sup>1</sup>

Thermal decomposition of	Approximate activation energy for heterogeneous reaction (g.-cal./g.-mol.).	Activation energy for homogeneous reaction (g.-cal./g.-mol.).
HI	25,000 on Au <sup>2</sup> 14,000 on Pt <sup>3</sup>	44,000
N <sub>2</sub> O	29,000 on Au <sup>4</sup> 32,500 on Pt <sup>5</sup>	58,500
NH <sub>3</sub>	42,040 on W <sup>6</sup> 32,000 to 42,000 on Mo <sup>7</sup> 47,000 on Os <sup>8</sup>	>80,000
CH <sub>4</sub>	55,000 to 60,000 on Pt <sup>9</sup>	>80,000

<sup>1</sup> Glasstone, Laidler and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., 1941, p. 390.<sup>2</sup> Hinshelwood and Prichard, J.C.S. 1925, **127**, 1552.<sup>3</sup> Hinshelwood and Burk, J.C.S. 1925, **127**, 2896.<sup>4</sup> Hinshelwood and Prichard, Proc. Roy. Soc. 1925, A, **109**, 211.<sup>5</sup> Hinshelwood and Prichard, J.C.S. 1925, **127**, 327.<sup>6</sup> Barrer, Trans. Faraday Soc. 1930, **32**, 490.<sup>7</sup> Kunsman, J. Amer. Chem. Soc. 1928, **50**, 2100.<sup>8</sup> Arnold and Burk, J. Amer. Chem. Soc. 1932, **54**, 23.<sup>9</sup> Schwab and Fliesch, Z. physikal. Chem. 1926, **121**, 189.

place with the larger activation energy. The function of the solid has been to replace the homogeneous mechanism, in which activation energy is accumulated by a collision process, by an alternative reaction path involving a much smaller activation energy. This is the typical property of a catalyst. The relationships may be summarised in the potential energy diagram of Fig. 2.

By using the transition-state method it is possible to determine the relative velocities of a heterogeneous reaction and the same homogeneous reaction under otherwise identical conditions (Glasstone, Laidler and Eyring, *op. cit.*, p. 389). Then

No. of molecules reacted heterogeneously  
No. of molecules reacted homogeneously

$$\frac{\text{per unit time per cm.}^2}{\text{per unit time per c.c.}} \simeq 10^{-12} \frac{\Delta E}{RT}$$

where  $\Delta E = E_{\text{hom.}} - E_{\text{het.}}$  in g.-cal. per g.-mol. transformed. Thus for the reactions to be comparable in velocity it would be necessary to

have a surface of  $10^{12}$  cm.<sup>2</sup> or else  $eRT$  would have to be  $\simeq 10^{12}$ , i.e.  $E_{\text{hom.}} > E_{\text{het.}}$ . At 500°K. with a surface of 1 cm.<sup>2</sup> and a volume of 1 c.c.  $\Delta E$  would need to be 27,000 g.-cal. per g.-mol.

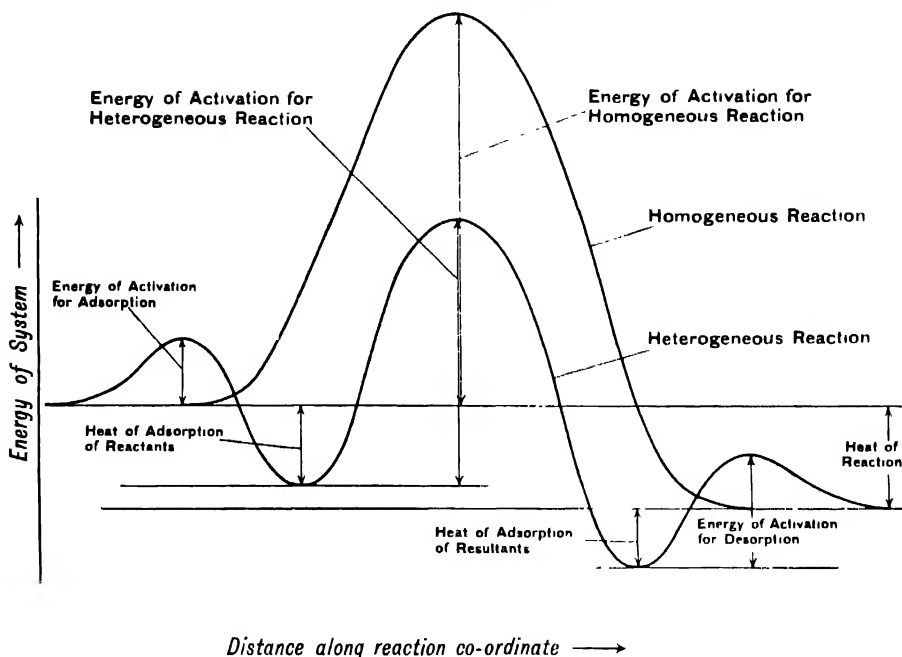
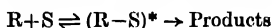


FIG. 2.—DIAGRAMMATIC COMPARISON OF ENERGY RELATIONS OF THE SAME REACTION OCCURRING BY HOMOGENEOUS AND HETEROGENEOUS MECHANISMS.

to obtain equality in rates. Such values of  $\Delta E$  are similar to  $(E_{\text{hom.}} - E_{\text{het.}})$  in Table IV.

(vi) **The Absolute Velocity of Heterogeneous Reactions.**—The calculation of absolute reaction velocities is essentially similar for heterogeneous and homogeneous reactions. For a unimolecular surface reaction, one may write:



where R denotes the reactant and S the site on which it is adsorbed. The star denotes that the reactant has received the activation energy needed for reaction (i.e. it is in the activated or transition state). The expression for the reaction velocity according to the calculations of Eyring (J. Chem. Physics, 1935, 3, 107), Evans and Polanyi (Trans. Faraday Soc. 1935, 31, 875) and others (Glasstone, Laidler and Eyring, *op. cit.*, Chapters I and IV) is

$$\text{Rate} = C_g C_s \frac{kT}{h} \frac{f^*}{F_{\theta} f_s} e^{-\frac{E}{RT}} \quad (9)$$

where  $C_g$  = the concentration of reactant molecules in the gas phase.

$C_s$  = the number of sites available for adsorption per unit area.

$k$  = the Boltzmann constant.

$h$  = Planck's constant.

$f^*$  = the partition function of the transition state complex, excluding the partition function for the co-ordinate in which decomposition occurs.

$f_s$  = the partition function of the adsorption sites.

$F_{\theta}$  = the partition function for unit volume of the gas.

$E$  = the energy required to produce the activated state.

The partition functions can be evaluated for certain simple systems, and since  $E$ ,  $C_s$  and  $C_g$  may be measured, the reaction rates may be calculated. Table V compares some observed and calculated reaction velocities. The procedure has equal success in calculating the velocity of oxidation of nitric oxide on glass, a bimolecular reaction.

TABLE V.—OBSERVED AND CALCULATED VELOCITY CONSTANTS OF UNIMOLECULAR SURFACE REACTIONS.<sup>1</sup>

Decomposition of	Surface.	T° K.	Specific reaction rate (sec. <sup>-1</sup> ).	
			Calc.	Obs.
PH <sub>3</sub>	Glass	684	$2.2 \times 10^{-8}$	$4.7 \times 10^{-7}$
HI	Pt	836	$1.2 \times 10^{-8}$	$1.0 \times 10^{-8}$
N <sub>2</sub> O	Au	1,211	$3.4 \times 10^{-8}$	$12.3 \times 10^{-8}$

<sup>1</sup> From data of Glasstone, Laidler and Eyring, *op. cit.*, Table XLI.

(vii) **Heterogeneous Reactions involving Isotopic Molecules.**—When the heavy hydrogen isotope was obtained in chemically useful quantities by progressive electrolysis of acidulated water (Washburn and Urey, Proc. Nat.

Acad. Sci. 1932, 18, 496; Lewis and MacDonald, J. Chem. Physics, 1933, 1, 341) the attention of chemists was directed to reactions involving isotopes and isotopic molecules. It then became apparent that *isotopes do not behave identically in chemical reactions* (Table XII). The differences are greater the more the mass ratio differs from unity, and is most marked with the isotopes of hydrogen. Some approximate mass ratios are:

$$\begin{array}{lll} \text{D} & 2.00; & {}^{18}\text{O} \\ \text{H} & {}^{16}\text{O} = 1.125; & {}^7\text{Li} \\ & & {}^6\text{Li} = 1.17; \\ & {}^{13}\text{C} & {}^{15}\text{N} \\ & {}^{12}\text{C} = 1.08; & {}^{14}\text{N} = 1.07. \end{array}$$

As the atomic weight rises the isotopic mass ratio approaches unity. This means that the chemical differences between  ${}^{207}\text{Pb}$  and  ${}^{206}\text{Pb}$ , for instance, will be too small to be detected.

Three factors contribute to differences in heterogeneous reaction velocity in isotopic systems:

(i) Differences in gas kinetic velocities, leading to different rates of bombardment of a surface, and contributing to differences in adsorption equilibrium.

(ii) Differences in zero-point energy. The lighter isotopic molecule has the higher zero-point energy, and is assisted in gaining the necessary activation energy by the amount of this energy. Therefore, other things being equal, the light isotopic molecule reacts more quickly than the heavy isotopic molecule (e.g.  $\text{H}_2$  and  $\text{D}_2$ ).

(iii) The tunnel effect. Quantum mechanics predicts that an atom may under certain conditions pass over an energy barrier from an initial to a final chemical configuration without acquiring the necessary activation energy. Light and heavy hydrogen are the only isotopes of mass small enough for this effect to be detected, but the phenomenon has not yet been observed in any heterogeneous or homogeneous isotopic reactions.

In Table VI are collected some differences in apparent energy of activation for heterogeneous reactions. The light isotopic molecule always reacts more rapidly, as the theory would predict. Moreover, the observed values of  $\Delta E$  are of the magnitudes calculated (Eyring and Sherman, J. Chem. Physics, 1933, 1, 345). On p. 219d are considered some other processes involving isotopes.

TABLE VI.—DIFFERENCES IN APPARENT ENERGY OF ACTIVATION FOR HETEROGENEOUS REACTIONS <sup>1</sup> INVOLVING ISOTOPIC MOLECULES.

Reaction.	$E$ (apparent) g.-cal per g.-mol.	$\Delta E$ from $\frac{k_u}{k_v} = e^{-\frac{\Delta E}{RT}}$ in g.-cal. per g.-mol.
$\text{H}_2 + 2\text{C}_{\text{solid}} \rightarrow 2\text{CH}$ surface	15,700	700 <sup>2</sup>
$\text{D}_2 + 2\text{C}_{\text{solid}} \rightarrow 2\text{CD}$ surface		
$2\text{NH}_3 \xrightarrow{W} \text{N}_2 + 3\text{H}_2$	42,400	800, 790 <sup>3</sup>
$2\text{ND}_3 \xrightarrow{W} \text{N}_2 + 3\text{D}_2$		890, 900
$2\text{PH}_3 \xrightarrow{W} 2\text{P} + 3\text{H}_2$	32,200	510, 550 <sup>3</sup>
$2\text{PD}_3 \xrightarrow{W} 2\text{P} + 3\text{D}_2$		
$12\text{H}_2\text{O} + \text{Al}_4\text{C}_3 \rightarrow 4\text{Al}(\text{OH})_3 + 3\text{CH}_4$	14,200	750 <sup>4</sup>
$12\text{D}_2\text{O} + \text{Al}_4\text{C}_3 \rightarrow 4\text{Al}(\text{OD})_3 + 3\text{CD}_4$		
$\text{CH}_4 + 3\text{C}_{\text{solid}} \rightarrow 4\text{CH}$ surface	$\geq 26,700$	780 <sup>2</sup>
$\text{CD}_4 + 3\text{C}_{\text{solid}} \rightarrow 4\text{CD}$ surface		
$\text{H}_2 + \text{CuO} \rightarrow \text{Cu} + \text{H}_2\text{O}$		400 <sup>5</sup>
$\text{D}_2 + \text{CuO} \rightarrow \text{Cu} + \text{D}_2\text{O}$		
Hydrogenation of styrol (Pd-BaSO <sub>4</sub> catalyst)		540 <sup>6</sup>
$\text{H}_2 - \text{D}_2 + \text{O}_2 \xrightarrow{\text{Ni}} \text{H}_2\text{O} - \text{D}_2\text{O}$		750 <sup>7</sup>
$\text{H}_2 - \text{D}_2 + \text{N}_2\text{O} \xrightarrow{\text{Ni}} \text{H}_2\text{O} - \text{D}_2\text{O} + \text{N}_2$		720 <sup>7</sup>
$\text{H}_2 - \text{D}_2 + \text{C}_2\text{H}_4 \xrightarrow{\text{Ni}} \text{C}_2\text{H}_6 - \text{C}_2\text{H}_4\text{D}_2$		700 <sup>7</sup>

<sup>1</sup> Data from Barrer, "Diffusion in and through Solids," Cambridge University Press, 1941, p. 188.

<sup>2</sup> Barrer, Trans. Faraday Soc., 1936, 32, 482.

<sup>3</sup> Barrer, *ibid.*, p. 490.

<sup>4</sup> Barrer, *ibid.*, p. 486.

<sup>5</sup> Melville and Rideal, Proc. Roy. Soc. 1936, A, 153, 89.

<sup>6</sup> Cremer and Polanyi, Z. physikal. Chem. 1932, B, 19, 443.

<sup>7</sup> Melville, J.C.S. 1934, 1243.

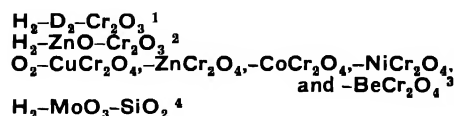
(viii) Activated Adsorption and Chemisorption as Heterogeneous Reactions.—When oxygen is sorbed by charcoal at moderate temperatures, the process is chemical and the oxygen cannot be recovered by evacuation and further heating, only oxides of carbon being

evolved. The process is an example of irreversible chemisorption. In other cases, however, the sorbed gas may be recovered at a higher temperature and under vacuum, yet the sorption occurs slowly and is chemical in nature (e.g.  $\text{H}_2$  by charcoal, graphite and diamond, at high tem-

peratures (Barrer, Proc. Roy. Soc. 1935, A, 149, 231; Trans. Faraday Soc. 1936, 32, 482; J.C.S. 1936, 1256)). For chemical adsorption, occurring reversibly and requiring an activation energy, the term *activated adsorption* has been proposed (Taylor, J. Amer. Chem. Soc. 1931, 53, 578; Barrer, *op. cit.*, p. 232).

The combustion of carbon has been studied extensively (reviewed by Mayers, Chem. Rev. 1934, 14, 31; also Faraday Society Discussion on "Chemical Reactions Involving Solids," Part IIc, Trans. Faraday Soc. 1938, 34, 1011); in furnace beds (Tu, Davis and Hottel, Ind. Eng. Chem. 1934, 26, 749); under low pressure conditions with small quantities of charcoal (Cassel, J. Amer. Chem. Soc. 1936, 58, 1309), graphite or diamond (Barrer, J.C.S. 1936, 1261); and using graphite filaments (Langmuir, J. Amer. Chem. Soc. 1915, 37, 1154; Meyer, Z. physikal. Chem. 1932, B, 17, 385). The kinetics have been observed under these various conditions with static and flowing gas atmospheres. Combustion may be governed at low temperatures by irreversible desorption rates of a chemically-held layer of oxygen. At high temperatures the rate of chemical reaction between oxygen and carbon can be the deciding factor, and at the most elevated temperatures, or in furnace beds at lower temperatures, the rate of inter-diffusion of gaseous reactants and resultants is the slowest process.

Activated adsorption has been studied in a number of instances. The chemical uptake of hydrogen by the various forms of carbon must be regarded as the first step in hydrogenation. To induce further reaction, however, catalysts and high pressures are necessary. Among the first activated adsorptions to be studied were reactions involving oxides ( $\text{Cr}_2\text{O}_3$ ,  $\text{ZnO}-\text{Cr}_2\text{O}_3$ ) (Taylor, J. Amer. Chem. Soc. 1931, 53, 578), but it is not certain to what extent these are reversible and therefore how far they are irreversible chemisorptions and how far activated adsorptions. To this class belong the following systems:



#### B. REACTIONS INVOLVING THE SOLID-LIQUID INTERFACE.

The solid-liquid interface is the seat of numerous technical reactions. The velocity of these reactions may be governed by the chemical processes at the interface, but equally often by diffusion of reactants or resultants to and from the interface. If chemical processes are slower, the reaction velocity is governed by considerations of the same kind as given on pp. 208, 209,

in systematising the kinetics of gas-solid reactions. There is the additional complication that a solvent medium is usually present, and that reactants and resultants compete for the surface with solvent molecules, and with other solutes. These may substantially modify the surface populations of the reactants. Moreover, diffusion in liquid media is much slower than in gases and therefore reaction kinetics in such systems are more often those of diffusion than in gas-solid reactions.

(i) Diffusion as a Rate-controlling Process.—Down any concentration gradient the rate of diffusion may be defined by

$$P = -D \frac{\delta c}{\delta x} \quad (10)$$

where  $P$  denotes the quantity of solute diffused per unit time,  $D$  is the diffusion constant, and  $\frac{\delta c}{\delta x}$  is the concentration gradient. The diffusion constant may be related to the mobility  $B$  (defined as the steady velocity of the particle moving through the solution under unit force) by the relation

$$D = \frac{RT}{N} B \quad (11)$$

The value of  $B$  for spherical particles large compared with the molecules of solvent is given by

$$B = \frac{1}{6\pi\eta r} \quad (12)$$

where  $r$  denotes the particle radius and  $\eta$  the viscosity of the medium. The law is not necessarily valid when the dimensions of solute and solvent molecules are similar, although it is frequently applied to such solutions. If it is assumed that the liquid solvent behaves as though it were quasi-crystalline<sup>1</sup> the diffusion constant may be evaluated by methods used for diffusion in solids (summarised by Barrer, *op. cit.*, Table 76) and is given by

$$D = \frac{d^2}{6} \nu \left( \frac{E}{RT} \right)^{(f-1)} \frac{1}{(f-1)!} e^{-\frac{E}{RT}} \quad (13)$$

where  $\nu$  is the vibration frequency of the solute atom in one quasi-equilibrium position,  $E$  is the energy of activation needed for it to jump to another such position distant  $d$  from it, and  $f$  denotes the number of degrees of freedom among which the activation energy may be distributed.

Noyes and Whitney (Z. physikal. Chem. 1897, 23, 689) first used diffusion theory to interpret their experimental work upon the solution rates of benzoic acid and lead chloride. Cylinders of these solids were rotated in water and the concentration of solute was determined as a function of time. They assumed that the water just in contact with the solid was saturated with solute, and that the concentration diminished linearly over a small distance  $\delta$  until it was substantially the concentration in the bulk of the stirred

<sup>1</sup> Taylor and Diamond, J. Amer. Chem. Soc. 1934, 56, 1821; Kohlschütter, Z. physikal. Chem. 1934, 170, 300.

<sup>2</sup> Pace and Taylor, J. Chem. Physics, 1934, 2, 578.

<sup>3</sup> Frazer and Heard, J. Physical Chem. 1938, 42, 855.

<sup>4</sup> Griffith and Hill, Proc. Roy. Soc., 1935, A, 148, 195; Hollings, Griffith and Bruce, *ibid.*, p. 186.

<sup>1</sup> There is considerable evidence in favour of this view, especially for associated liquids near their freezing points.

solution. Then the simple diffusion theory gives (Nernst, *ibid.* 1904, 47, 52):

$$\text{Rate of solution} = \frac{DA}{\delta} (C_s - C) \quad (14)$$

Where  $A$  denotes the area of the solid,  $C_s$  and  $C$  are the saturation concentration of solute and its concentration in the stirred solution, respectively, and  $V$  denotes the volume of the solution. Integrating

$$\ln \frac{C_s}{C_s - C} = kt \quad (15)$$

where  $k = \frac{AD}{V\delta}$  and  $t$  denotes the time. From the measured values of  $k$  and  $D$ ,  $\delta$  varies in typical cases from  $20\mu$  to  $50\mu$  (Brunner, *ibid.* 1904, 47, 56). Evidence supporting the diffusion layer theory has since been obtained by various workers for chemical as well as physical processes (Van Name and Edgar, *ibid.* 1910, 73, 97; Van Name and Bosworth, *Amer. J. Sci.* 1911, 32, 207; Van Name and Hill, *ibid.* 1913, 36, 543). It should be emphasised that the form of the relationship does not depend upon the conception of a diffusion layer of definite thickness  $\delta$ . Equations of similar form can be derived without its use. Further, the velocity of solution or reaction may depend upon the crystal face exposed and can be altered by addition of other solutes. The surfaces exposed soon become eroded and this may modify the value of  $A$ , and cause trends in  $k$ , although the factor this introduced was much less than the roughness factor of the surface (for a discussion of the literature, see Taylor, "Treatise on Physical Chemistry," Macmillan & Co., 1931, Vol. II, p. 1028).

Certain characteristics of reactions controlled by diffusion have emerged:

- (1) The reaction rate varies with the rate of stirring ( $r$ ) of the solvent:  
Reaction velocity  $= kr^n$   
where  $n < 1$ .
- (2) Factors altering the viscosity  $\eta$  of the medium alter  $D$ , and so  $k = \frac{AD}{V\delta}$ .
- (3) Temperature strongly influences the viscosity.

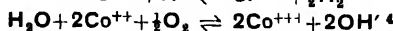
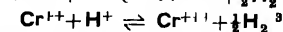
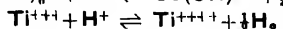
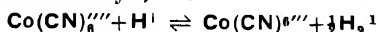
The viscosity decreases and so the diffusion constant increases as the temperature rises, thus giving a positive temperature coefficient to the reaction velocity. The temperature coefficient of diffusion is usually much smaller than the temperature coefficient of a chemical reaction and therefore the reaction rate is less sensitive to temperature in a diffusion-controlled process. In water the temperature coefficients of  $D$  for various simple electrolytes<sup>1</sup> at room temperatures range from 1.19 to 1.28 per  $10^\circ$  rise (e.g. Öholm, *Z. physikal. Chem.* 1904, 50, 309; *ibid.* 1910, 70, 378; Medd. K. Vetenskapsakad. Nobel-Inst. 1912, 2, Nos. 23, 24, 26). As the size of the solute molecules or ions increases, however, so does the temperature coefficient of diffusion. Nevertheless, these temperature co-

efficients are below those for chemical reactions which are usually not less than 2 per  $10^\circ\text{C}$ . rise at room temperature. A useful criterion of a reaction limited by diffusion is therefore a temperature coefficient not above 1.5 per  $10^\circ\text{C}$ . rise. The same reaction may begin under certain conditions as one controlled by diffusion, and change, under other conditions, to one controlled by chemical reaction. Thus when certain metals were dissolved in HCl the temperature coefficients altered with concentration in a typical instance as follows (Guldberg and Waage, Ostwald's Klassiker, No. 104, 52):

Normality of HCl	1.3	2.0	2.6	4	8
Rate at $18^\circ\text{C}$ .	1.58	1.68	1.70	2.44	3.23
Rate at $0^\circ\text{C}$ .					

Again, on platinum black the decomposition of  $\text{H}_2\text{O}_2$  has a temperature coefficient of 1.28 per  $10^\circ\text{C}$ . rise. On colloidal platinum, by contrast, the temperature coefficient becomes "chemical" in magnitude ( $\approx 2$  per  $10^\circ\text{C}$ .) (cf. W. M. McC. Lewis, "A System of Physical Chemistry," Longmans, Green & Co., 1923, Vol. I, pp. 458 *et seq.*). This appears to be a general difference between massive and colloidal catalysts which has not yet been satisfactorily explained. It is possible that Brownian movement removes the colloidal particle from its atmosphere of reactants, thus continually exposing it to fresh supplies of reactants independently of diffusion.

According to the diffusion theory, the reaction rate follows a pseudo first-order rate equation. Typical reactions of this kind, where equilibria are established in presence of massive platinum as catalyst, are:



Reaction proceeds to completion in other instances, such as:

Reactions of metals (Zn, Cd, Hg, Cu, Ag) with  $\text{I}_2$  in KI solution.<sup>5</sup>

Reaction of Hg with  $\text{Br}_2$ .<sup>6</sup>

Solution of MgO in benzoic, acetic and hydrochloric acid solutions.<sup>6</sup>

Solution of  $\text{CaCO}_3$  in hydrochloric acid.<sup>6</sup>

Solution of benzoic acid,  $\text{PbCl}_2$ ,  $\text{CH}_3\cdot\text{CO}_2\text{Ag}$ , in water.<sup>6</sup>

(ii) Chemical Reaction as a Rate-controlling Process.—Most reactions in solution occurring at the surfaces of inorganic or organic colloids have the high temperature coefficients appropriate to chemical processes. Some systems in which diffusion should govern the rate of reaction are not, in fact, so controlled. The solution of Al, Cd, and Sn in hydrochloric acid may occur at rates independent of the diffusion

<sup>1</sup> Manchot and Herzog, *Ber.* 1900, 33, 1742.

<sup>2</sup> Diethelm and Foerster, *Z. physikal. Chem.* 1908, 62, 129; Dgnham, *ibid.* 1910, 72, 841.

<sup>3</sup> Jablczynski, *ibid.* 1908, 64, 748.

<sup>4</sup> Oberer, *Diss.*, Zurich, 1903.

<sup>5</sup> Van Name and Edgar, *Z. physikal. Chem.* 1910, 73, 97.  
<sup>6</sup> Cf. Taylor, *op. cit.*, Vol. II., p. 1032; Brunner, *Z. physikal. Chem.* 1904, 47, 56.

<sup>1</sup> For an electrolyte  $D = \frac{2UV}{U+V} \frac{RT}{4\pi}$  where  $U$  and  $V$  are the mobilities of cation and anion, respectively.



process and with chemical temperature coefficients (Centnerszwer, Z. physikal. Chem. 1929, 141, 297). Formic acid solutions decompose at the surface of rhodium with a temperature coefficient of 2 (Blackadder, Z. physikal. Chem. 1912, 81, 385) and also palladium sponge decomposes aqueous  $\text{Na}_2\text{HPO}_4$  with the typical chemical temperature coefficient of 2 per  $10^\circ\text{C}$ . rise at room temperature (Sieverts and Peters, Z. physikal. Chem. 1916, 91, 199).

To interpret the kinetics one may employ the Langmuir isotherm as indicated on p. 208a and p. 208c.

$$\frac{x}{m} = \frac{kac}{1+ac}$$

where  $\frac{x}{m}$  denotes the amount of a solute adsorbed

per unit mass of catalyst,  $k$  and  $a$  are constants and  $c$  is the bulk phase concentration of solute. If there is competition for the surface by two molecular species one may write for each (cf. p. 210a)

$$\frac{x_1}{m} = \frac{k_1ac_1}{1+ac_1+bc_2}$$

$$\frac{x_2}{m} = \frac{k_2bc_2}{1+ac_1+bc_2}$$

The interpretation of reaction kinetics is not as complete as at the gas-solid interface (Tables I, II and III), but typical kinetics are summarised in Table VII. It is possible to offer alternative suggestions such as No. 2, Table III, and No. 4, Table II, to explain why  $x_2$  is independent of  $x_1$  in No. 5, Table VII. Reactions at the liquid-

TABLE VII.—REACTION KINETICS AT THE LIQUID-SOLID INTERFACE.

No.	Conditions.	Rate equation.	Examples.
1.	Single reactant weakly adsorbed.	$-\frac{dc}{dt} = k'x$ $= kc$ ( $x$ denotes amount adsorbed, $c$ denotes concentration of reactant in solution).	Hydrolysis of lactose and sucrose by enzymes at small sugar concentrations. <sup>1</sup> Decomposition of $\text{H}_2\text{O}_2$ on colloidal metals. <sup>2</sup> Decomposition of $\text{H}_2\text{O}_2$ by hæmase. <sup>3</sup>
2.	Single reactant strongly adsorbed.	$-\frac{dc}{dt} = k'x$ $= k$ (surface saturated).	Hydrolysis of sugars by enzymes at high sugar concentrations. <sup>1</sup> Decomposition of $\text{H}_2\text{O}_2$ by some colloidal or finely divided oxides in alkaline media. <sup>2</sup>
3.	Single reactant moderately adsorbed.	$-\frac{dc}{dt} = k'x$ $= \frac{kac}{1+ac}$ $\approx Kc^n$ ( $n < 1$ )	Decomposition of formic acid solutions on Rh. <sup>4</sup>
4.	Two reactants, one strongly adsorbed, the reaction governed by diffusion of the other.	$-\frac{dc}{dt} = k'c_1x_2$ $= kc_1$ (since surface saturated with component 2).	$\text{Ti}^{+++} + \text{H}^+ \rightleftharpoons \text{Ti}^{++++} + \frac{1}{2}\text{H}_2$ catalysed by Pt black in both directions ( $\text{H}_2$ strongly adsorbed). <sup>5</sup> Catalytic hydrogenations of many compounds containing ethylenic double bonds (liquid organic molecule strongly adsorbed). <sup>6</sup>
5.	Two reactants, one moderately adsorbed, the other present in great excess.	$-\frac{dc}{dt} = k'x_1x_2$ $= \frac{kac_1}{1+ac_1}$ if $x_2$ does not alter during the course of reaction, i.e. $c_2$ substantially constant.	$\text{NaH}_2\text{PO}_4 + \text{H}_3\text{O}^+ \rightarrow \text{NaH}_2\text{PO}_3 + \text{H}_2$ <sup>7</sup> (palladium black as catalyst).

<sup>1</sup> Armstrong, Proc. Roy. Soc. 1904, 73, 508.

<sup>2</sup> Bredig and Von Berneck, Z. physikal. Chem. 1899, 31, 258; Bredig and Ikeda, *ibid.* 1901, 37, 1.

<sup>3</sup> Senter, *ibid.* 1905, 61, 673.

<sup>4</sup> Blackadder, *ibid.* 1912, 81, 385.

<sup>5</sup> Denham, *ibid.* 1910, 72, 641.

<sup>6</sup> E.g. Armstrong and Hilditch, Proc. Roy. Soc. 1919, A, 98, 137; 1920, A, 98, 27; 1921, A, 100, 240.

<sup>7</sup> Sieverts and Peters, Z. physikal. Chem. 1916, 91, 199.

solid interface are susceptible to poisons in the same way as those at the gas-solid interface. For instance, the catalytic hydrogenation of hydrocyanic acid to methylamine at the surface of platinised platinum is almost inhibited by excess of cyanide ion (Barrer, Thesis, University of New Zealand, 1931). Again, the decomposition of hydrogen peroxide is strongly poisoned by minimal quantities of several reagents (Table VIII).

TABLE VIII.—POISONING OF  $\text{H}_2\text{O}_2$  DECOMPOSITION.<sup>1</sup>

Reaction on:	Poison used.	Quantity of poison to reduce rate to half the unpoisoned rate.
Colloidal Pt sols containing $10^{-5}$ g-atoms of Pt per litre.	HCN	$5 \times 10^{-8}\text{N}$
	ICN	$7 \times 10^{-6}\text{N}$
	$\text{I}_2$	$7 \times 10^{-6}\text{N}$
	$\text{HgCl}_2$	$2.5 \times 10^{-6}\text{N}$
Blood catalase . .	HCN	$1 \times 10^{-6}\text{N}$
	$\text{I}_2$	$2 \times 10^{-6}\text{N}$
	$\text{H}_2\text{S}$	$1 \times 10^{-6}\text{N}$
	$\text{HgCl}_2$	$5 \times 10^{-7}\text{N}$

<sup>1</sup> Cf. W. C. McI. Lewis, "A System of Physical Chemistry," Longmans, Green & Co., 1925, Vol. I, p. 455.

The poisoning action is often to be explained, just as in gas-solid reactions, by a strong preferential adsorption of the poison at the catalytic surface. That powerful adsorption of hydrocyanic acid occurs on platinum is further indicated by the observation that its catalytic reduction to methylamine is of apparent zero order with respect to HCN, i.e. the catalytic surface is maintained saturated with HCN.

(iii) **Base-Exchange Reactions.**—An important series of liquid-solid reactions involves base exchange. Base exchangers include synthetic gel zeolites, natural zeolites, clays, green-sand, organic substances such as humic acids, proteins, wood and coal products and basic and acidic synthetic resins. For some purposes at least the resins bid fair to displace the inorganic base exchangers, for they may be prepared in forms stable to acids and alkalis, resistant to heat, of high base exchange capacity, and rapid in action (R. Myers, Eastes, and F. Myers, Ind. Eng. Chem. 1941, 33, 697). Processes involving base-exchangers include water-softening, total demineralising of water, purification of sugar juices, and the recovery of small amounts of valuable solutes, from electroplating wastes, of alkaloids and amino acids, or of cuprammonium from rayon-spinning waste liquors. Exchangers have also been used in analysis, separation of isotopes (see Table XIII), as solid buffers for  $p_{\text{H}}$  control in the fermentation industries, and in the preparation of  $\text{NaNO}_3$  from  $\text{Ca}(\text{NO}_3)_2$  and sea-water. Many new applications will follow further technical development of the subject. (For a brief summary, see Walton, J. Franklin Inst. 1941, 232, 305.)

In technology the exchange process is usually carried out in flow systems. The solution containing reactants enters one end of a column of exchanger and flows out at the other, depleted of reactants. When exhausted the exchanger is regenerated by reversing the rôles of the cations involved in the first stage. It is unfortunate that the kinetic studies on these processes are at best semi-quantitative. Reaction may be confined to the surface layer, or diffusion into the gel or crystal may cause the exchanging cation to displace entirely the cation initially in the solid. The kinetics are then governed by diffusion within the solid and the equation

$$\text{Amount of exchange} = k\sqrt{t}$$

would apply to a first approximation. It is improbable that complete base-exchange occurs in many systems unless a far longer period is allowed for equilibrium to be established than is economically expedient. For most purposes, however, reaction on exchangers of practical importance is soon negligibly slow and it is then observed empirically that <sup>1</sup>, after a sufficient time  $t$  has elapsed,  $\left(\frac{c_1}{c_2}\right)_{\text{solid}} = k \left(\frac{c_1}{c_2}\right)_{\text{solution}}^p$  where  $k$  and the exponent  $p$  are constants and  $c_1$  and  $c_2$  are the concentrations of the exchanging species in both solid and liquid phases. The law of mass action would predict for simple equilibrium that  $p=1$ . Table IX, which gives values of  $k$  and  $p$  for a few typical systems, shows that  $p$  usually differs considerably from unity. One explanation may be that true equilibrium is not normally established.

Further qualitative observations have been made on crystalline minerals. Those showing

TABLE IX.—CONSTANTS IN THE EQUATION

$$\left(\frac{c_1}{c_2}\right)_{\text{solid}} = k \left(\frac{c_1}{c_2}\right)_{\text{solution}}^p$$

The subscript 2 refers to the cation originally in the zeolite and 1 to the added ion.

Reaction system (X denotes the zeolite substrate).	$p$ .	$k$ .	Concentration of added ion.
$\text{NH}_4\text{X}$ (fusion product) + $\text{Na}^+$ . . .	0.67	0.35	—
$\text{NH}_4\text{X}$ (fusion product) + $\text{K}^+$ . . .	0.72	1.0	—
Li-bentonite + $\text{NH}_4^+$ .	0.80	1.25	—
K-bentonite + $\text{NH}_4^+$ .	1.1	0.5	—
$\text{NaX}$ (gel product) + $\text{Ca}^{++}$ . . .	0.63	0.67	0.25N
$\text{NaX}$ (gel product) + $\text{Ba}^{++}$ . . .	0.55	1.78	0.25N
K-green sand + $\text{Ca}^{++}$ .	0.6	0.6	1.00N
Ba-casein + $\text{Na}^+$ . . .	0.7	0.0045	—
Ca-casein + $\text{Ba}^{++}$ . .	0.75	1.2	—
Ba-casein + $\text{Ca}^{++}$ . .	0.45	0.6	—

<sup>1</sup> Other types of equation have also been proposed. See, for example, Wiegner, J.S.C.I. 1931, 50, 65T.

base-exchange can be grouped into three categories: fibrous structures, plate-like or micaceous structures and three-dimensional networks. The more open the network the more rapid is the base exchange, whilst the theory of diffusion requires, and experiment shows, that the rate of exchange is usually increased by increasing the state of subdivision of the particles (*cf.* Zoch, *Chem. Erde*, 1915, 1, 1–55). Two typical classifications of base exchange *capacity*, to some extent confused with base exchange *velocity* in certain cases (*cf.* Table IX), are given in Tables X and XI.

TABLE X.—CLASSIFICATION OF MINERALS AS BASE-EXCHANGERS.<sup>1</sup>

High base-exchange.	Moderate base-exchange.	Low or negligible base-exchange.
Montmorillonite ( <i>b</i> ).	Several zeolites ( <i>a</i> , <i>b</i> , <i>c</i> ).	Pyrophyllite ( <i>b</i> ).
Beldellite ( <i>b</i> ).	Micas ( <i>b</i> ).	Kaolinite ( <i>b</i> ).
Halloysite ( <i>b</i> ).	Chlorites ( <i>b</i> ).	Non-aluminous amphiboles ( <i>a</i> )
Several zeolites ( <i>a</i> , <i>b</i> , <i>c</i> ).	Aluminous amphiboles ( <i>a</i> )	Non-aluminous pyroxenes ( <i>a</i> ).
	Aluminous pyroxenes ( <i>a</i> ).	Apophyllite ( <i>b</i> ).
	Leucite ( <i>c</i> ).	

<sup>1</sup> Brammall and Leech, *Sci. J. Roy. Coll. Sci.* 1938, 8, 43; Edelmann, *Trans. Third Internat. Cong. Soil Sci.* 1966, 3, 97.

- (*a*) Fibrous structures  
(*b*) Lamellar structures.  
(*c*) Three-dimensional networks.

TABLE XI.—CLASSIFICATION OF MINERAL EXCHANGERS.<sup>1</sup>

Mineral.	Volume per O atom.	Cation exchange.
Garnet ( <i>c</i> ) . . . . .	15.4cu. A.	None
Muscovite ( <i>b</i> ) (a mica) .	19.2	Slight
Orthoclase ( <i>c</i> ) (a feldspar) . . . . .	23	Slight
Nosean ( <i>c</i> ) . . . . .	23.1	Fair
Ultramarine ( <i>c</i> ) . . . . .	23.1	Very good
Apophyllite ( <i>b</i> ) . . . . .	26.8	Fair
Natrolite ( <i>a</i> ) . . . . .	28.0	Very good
Glauconite . . . . .	28	Excellent

<sup>1</sup> Walton, *J. Franklin Inst.* 1941, 232, 305

- (*a*) Fibrous structures.  
(*b*) Lamellar structures.  
(*c*) Three-dimensional networks.

Table X shows that the kind of crystal structure does not govern the velocity and extent of base exchange, save indirectly by conditioning the openness of the lattice. The latter is the vital factor and Table XI attempts to indicate a measure of the openness by giving the atomic volume available per oxygen atom in the lattices of some base-exchanging minerals. The method gives correctly the qualitative order of ease of base-exchange. Base-exchange experiments with crystalline minerals such as zeolites must be continued for periods of days or months to reach completion, and approach to this state

asymptotic. (For a survey of base exchange data, *see* Doelter, "Handbuch der Mineralchemie," Bd. II, 1 Hälfte, 1914, p. 93; Bd. II, iii, 1921, pp. 1–416.) If the solute does not decompose at high temperatures, the hydrothermal method of digesting the zeolite at 100–200°C. with the salt solution in a sealed system causes acceleration of the reaction. (A summary of Lemberg's and Thugutt's extensive researches using this method is given by Schneiderhöhn, *Jahrb. Min. Beil.-Bd.* 1914, 40, 163. Base-exchange in ultramarines is discussed by Jaeger, *Trans. Faraday Soc.* 1929, 25, 320.) At still higher temperatures the zeolite may be heated with a fusible or volatile salt (*e.g.*  $\text{NH}_4\text{Cl}$ ) with further acceleration of reaction in some instances. (Method largely developed by Clarke and Steiger, in a series of papers from 1899–1905, *e.g.* Clarke, *Z. anorg. Chem.* 1905, 46, 197.)

#### C. REACTIONS INVOLVING THE GAS-LIQUID INTERFACE.

Processes involving the gas-liquid or vapour-liquid interface may be either physical or chemical. Physical reactions of solution and evolution of vapours from liquids are fundamentally important in industry, for they control rates of approach to the steady state in distillation, or solvent extraction processes. The industrial still may be idealised as a column containing a number of perforated plates. These hold up a small amount of liquid continually washed by ascending vapours. The latter in their turn partly condense and run back from plate to plate. Eventually by this process of washing and condensation a steady state is reached with volatile components predominating at the top of the still and the less volatile components at the bottom. This steady state is established quite slowly, and the more slowly the larger the total hold-up of vapour and liquid along the height of the column, so that a good still is designed to minimise this hold-up. For practical purposes the still with total reflux is converted into one with a definite forward flow, by withdrawing liquid or vapour slowly from the top of the still. The separation obtained depends upon the number of "theoretical plates" (*see above*) which the still may be said to contain. In theory the separation may be made as complete as desired by increasing the number of plates, but in practice this will reduce the rate of establishing the steady-state separation of components in the top and bottom of the column.

Chemical reactions at the gas-liquid interface may be exchange processes in counter-current systems basically not unlike the still described above, or they may be changes confined primarily to the gas-liquid phase boundary. These types of chemical change will now be discussed.

(i) **Exchange Reactions.**—Such reactions have become important recently in separating isotopic mixtures, largely in the hands of Urey and his co-workers (summarised by Urey, *Rep. on Prog. Phys.* 1939, 6, 48). Isotopes have slightly different chemical reactivities, as noted

on p. 213*d*. Equilibria in which gas and liquid isotopic mixtures participate give (Table XII) equilibrium constants which differ slightly from unity. The separation factors have proved sufficient however, to separate isotopes effectively by use of two-phase counter-current methods, either non-regenerative or regenerative in type. The method, with modifications, has succeeded, or partially succeeded, in the instances given in Table XIII.

TABLE XII.—ISOTOPIC EQUILIBRIA.<sup>1</sup>

Reaction.	Equilibrium constants :		
	273.1°K.	298.1°K.	600°K.
$\frac{1}{2}\text{S}^{16}\text{O}_2 + \text{H}_2^{18}\text{O} \rightleftharpoons \frac{1}{2}\text{S}^{18}\text{O}_2 + \text{H}_2^{16}\text{O}$ . . . . .	1.034	1.028	1.003
$\frac{1}{2}\text{C}^{16}\text{O}_2 + \text{H}_2^{18}\text{O} \rightleftharpoons \frac{1}{2}\text{C}^{18}\text{O}_2 + \text{H}_2^{16}\text{O}$ . . . . .	1.064	1.054	1.014
$\frac{1}{2}\text{H}_2^{16}\text{O} + \text{H}_2^{18}\text{O} \rightleftharpoons \text{H}_2^{18}\text{O} + \text{H}_2^{16}\text{O}$ . . . . .	1.024	1.020	1.003
$^{12}\text{CO} + ^{12}\text{CO}_2 \rightleftharpoons ^{12}\text{CO} + ^{13}\text{CO}_2$ . . . . .	1.098	1.086	1.029
$\frac{1}{2}\text{Cl}_2^{35} + \text{H}^{37}\text{Cl} \rightleftharpoons \frac{1}{2}\text{Cl}_2^{37} + \text{H}^{35}\text{Cl}$ . . . . .	1.004	1.003	1.00015
$\frac{1}{2}\text{Br}_2^{79} + \text{H}^{81}\text{Br} \rightleftharpoons \frac{1}{2}\text{Br}_2^{81} + \text{H}^{79}\text{Br}$ . . . . .	1.0005	1.0004	0.99997
$\frac{1}{2}\text{N}_2 + ^{15}\text{NO} \rightleftharpoons \frac{1}{2}\text{N}_2 + ^{14}\text{NO}$ . . . . .	1.016	1.015	1.0077
$^6\text{LiH} + ^7\text{Li} \rightleftharpoons ^7\text{LiH} + ^6\text{Li}$ . . . . .	1.028	1.025	1.008

<sup>1</sup> Urey and Greiff, J. Amer. Chem. Soc. 1935, 57, 321.

TABLE XIII.

Phases	Method.	Isotopes partially separated.
Liquid-Solid . . .	Saline solutions were percolated through columns of Na zeolite. The procedure was that of chromatographic analysis. Total reflux was not obtained. <sup>1</sup>	<sup>7</sup> Li concentrated in leading sample of LiCl solution, <sup>6</sup> Li concentrated in zeolite. <sup>14</sup> N concentrated in leading sample of NH <sub>4</sub> Cl solution. <sup>39</sup> K concentrated in leading sample of KCl solution.
Liquid-Liquid . . .	Exchange reaction proceeded between Li amalgam and LiCl in anhydrous CH <sub>3</sub> ·OH. Amalgam dropped through column of alcoholic LiCl 18 metres long. At the bottom the Li in the Li amalgam was converted to LiCl in alcohol and fed into base of column. System arranged to give total reflux. <sup>2</sup>	<sup>7</sup> Li concentrated in the amalgam, <sup>6</sup> Li in LiCl.
Gas-Liquid . . .	Ammonium salt solution in water flowed down through a fractionating column. NH <sub>3</sub> gas was liberated at the bottom by boiling with NaOH, and the NH <sub>3</sub> passed upward through column. System arranged to give total reflux. <sup>3</sup>	<sup>15</sup> N <sup>14</sup> N = 2.5% instead of 0.38%, using (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> as ammonium salt. <sup>15</sup> N concentrated in bottom of column.
Gas-Liquid . . .	HCN gas was fed into the bottom of the column. At the top it was absorbed in NaOH and the NaCN passed down the column. Total reflux obtained. <sup>4</sup>	Concentration of <sup>13</sup> C in gas phase at top of column. Concentration of <sup>12</sup> C in liquid phase at bottom of column.

<sup>1</sup> T. Taylor and Urey, J. Chem. Physics, 1938, 6, 429.

<sup>2</sup> Lewis and MacDonald, J. Amer. Chem. Soc. 1930, 52, 2519.

<sup>3</sup> Urey, Huffmann, Thode and Fox, J. Chem. Physics, 1937, 5, 856.

<sup>4</sup> Roberts, Thode and Urey, J. Chem. Physics, 1939, 7, 187; Urey, Mills, Roberts, Thode and Huffmann, *ibid.*, p. 138.

In the systems of Table XIII used for partial separation of nitrogen isotopes, carbon isotopes and lithium isotopes by total reflux, a very long time would be needed for the steady-state separations to be established. This militates against large separations in reasonable times. However, the cascade system of Fig. 3 will produce a high concentration of  $^{15}\text{N}$  in a relatively short interval. In the original system three separation units were employed. At F, ammonium nitrate entered unit 1, which was analogous in principle to the column described in Table XIII for the separation of  $^{14}\text{N}$  and  $^{15}\text{N}$ . In this unit the isotopic abundance ratio was

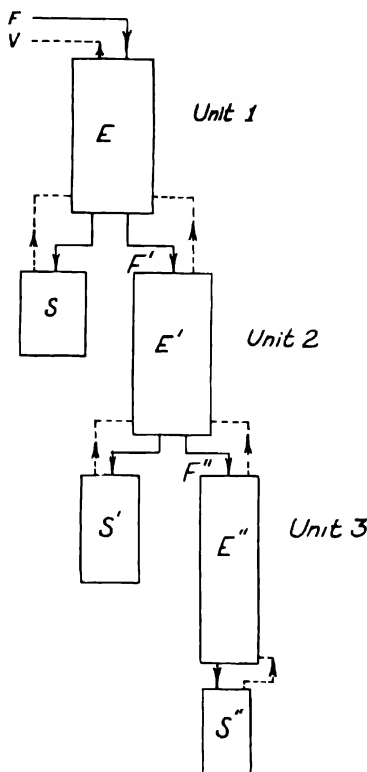
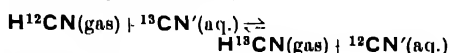


FIG. 3.—THREE-UNIT CASCADE SYSTEM FOR SEPARATION OF NITROGEN ISOTOPES.<sup>1</sup>

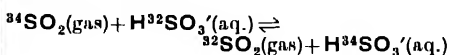
altered seven-fold. Six-sevenths of the flow was diverted from E to S, where boiling with NaOH served to liberate ammonia which in turn passed upwards through E and out at V. It was then converted to  $\text{NH}_4\text{NO}_3$  and returned to E at F. The remaining sixth entered the second unit at F' where the isotopic ratio was altered nine-fold. About eight-ninths of the total solution was passed to S' where boiling NaOH solution liberated ammonia which was returned through E' and E. The remaining one-ninth was passed into the third unit E'' where the abundance ratio was altered a further

eleven-fold. All this fraction was fed into S'' where boiling NaOH solution again liberated ammonia which was fed back into unit 3 and passed up through the whole system. Each unit consisted of glass columns of suitable heights varying from 24 m. (1st unit) to 7.5 m. (3rd unit) and packed with Berl saddles or Fenske helices, all of glass. A maximum concentration of 72.8%  $^{15}\text{N}$  was obtained and the net transport of  $^{15}\text{N}$  from ordinary nitrogen to samples ranging from 0.57 to 70.6%  $^{15}\text{N}$  was 0.75 g. per day. (Thode, Gorham and Urey, J. Chem. Physics, 1938, 6, 296; Thode and Urey, *ibid.* 1939, 7, 34.)

The cascade method has also succeeded in producing concentrations as high as 22% of  $^{13}\text{C}$  at the rate of 0.1 g. per day. (Urey, Rep. on Prog. Phys. 1939, 6, 62). The exchange reaction used was (cf. Table XIII):



Finally, the reaction



has served partly to resolve sulphur isotopes (Thode, Gorham and Urey, J. Chem. Physics, 1938, 6, 296; Stewart and Cohen, *ibid.* 1940, 8, 904).

#### (ii) Reactions confined to the Interface.

—Some reactions occur only or primarily at a liquid-vapour interface. The reaction between hydrogen and sulphur is believed to proceed in part in this way (Norris and Rideal, J.C.S. 1922, 123, 696; *ibid.* 1923, 123, 1689). The decomposition of methanol occurred as readily on liquid zinc as on zinc just below the melting-point (Steacie and Elkin, Proc. Roy. Soc. 1933, A, 142, 457; Canad. J. Res. 1934, 11, 47). The chief interest, however, centres upon reactions of a solute with insoluble monolayer films situated at the interface.

Oleic and *cis*-petroselinic acids form insoluble monolayer films which are attacked at the double bond by dilute acid permanganate (Hughes and Rideal, Proc. Roy. Soc. 1933, A, 140, 253). The reaction occurs more easily when the films are dilute, since then the molecule lies flat on the surface and the double bond is accessible to chemical attack. When the molecule is oriented vertically by compression of the monolayer, the double bond is not readily accessible and reaction is slow. Reactions of hydrolysis have also been observed, both of simple esters and of  $\gamma$ -hydroxy-stearo-lactone, on alkaline substrates (e.g. Alexander and Schulman, *ibid.* 1937, A, 161, 115). At constant surface pressure and alkali concentrations the latter reaction was of the first order with respect to the lactone and had a similar energy of activation (12,500 g.-cal. per g.-mol.) to the bulk phase reaction.

Auto-oxidation of  $\beta$ -elaeostearin and its maleic anhydride addition compound has been studied (Gee and Rideal, *ibid.* 1935, A, 153, 116; Gee, p. 129) and it was found that the oxidation velocity decreased at higher film compression, just as with oleic acid. Some film reactions are of obvious biological importance. Thus tannins combine with a protein monolayer (cf. Adam,

<sup>1</sup> After Urey, Rep. on Prog. Phys. 1939, 6, 61.

"Physics and Chemistry of Surfaces," Oxford University Press, 1938, p. 97), and snake venoms attack lecithin by removing a long chain fatty acid group (Hughes, *Biochem. J.* 1935, **29**, 437). A very striking phenomenon is the influence of the most minute traces of metallic cations upon the nature of surface films and upon reactions involving the films (Harkins and Myers, *Nature*, 1937, **139**, 367). The results available are fragmentary, but it appears that certain cations may influence the photolysis of stearic amide films (Rideal and Mitchell, *Proc. Roy. Soc.* 1937, **A**, **159**, 206) and reactions of a  $\alpha$ -hydroxystearic acid, stearic amide and proteins (Harkins and Myers, *Nature*, 1937, **139**, 367; Rideal, Mitchell and Schulman, *ibid.* 1937, **139**, 625). It may be presumed that the cations are adsorbed under the monolayer, altering its physical state or chemical reactivity in ways not yet understood.

Films exposed to the action of solutes may be collected and subjected to qualitative chemical examination. Nitrocellulose films exposed to sodium hydroxide solution and scraped off the surface by a glass rod were thus proved to have been denitrated (Adam, *Trans. Faraday Soc.* 1933, **29**, 96). Langmuir and Schaefer (*J. Amer. Chem. Soc.* 1936, **58**, 284) found that dilute  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  reacted with monolayers of fatty acid to give calcium and barium soaps if the  $p_H$  was sufficiently high. Other reactions at the gas-liquid interface are adequately reviewed by Adam ("Physics and Chemistry of Surfaces," Oxford University Press, 1938, pp. 95 *et seq.*).

#### D. REACTIONS INVOLVING THE LIQUID-LIQUID INTERFACE.

Few quantitative studies have been made of reaction rates in liquid two-phase media, although such systems are of the greatest importance in applied chemistry. The two liquids may be interdispersed as droplets, yielding emulsions, or they may be in the form of quiescent layers. Solvent extraction, soap-making, nitration and sulphonation are examples of large-scale processes where the velocity is of paramount importance. In these systems, the reaction zone often extends beyond the interface because the two liquids may be mutually soluble or the reactants may be distributed between them. The reactants may interact appreciably in one medium only, or both media may be active.

(i) **The Velocity of Establishing Distribution Equilibria.**—Studies on the rate of establishment of distribution equilibrium have led to seemingly contradictory conclusions. On the one hand, Berthelot and Jungfleisch (*Ann. Chim. Phys.* 1872, [iv], **26**, 396, 408) found that the distribution equilibrium of iodine and bromine between water and carbon disulphide required several hours to be established; while on the other hand Nernst (*Z. physikal. Chem.* 1891, **8**, 119) remarked upon the rapidity and certainty with which equilibrium was reached. Big differences may be due, however, to the extent of mixing and mechanical agitation. A solute introduced into one quiescent liquid layer requires many days to distribute itself uni-

formly and at equilibrium between the first layer and a second quiescent liquid layer.

(ii) **Reaction Occurring in One Liquid Phase Only.**—The simplest of liquid-liquid reactions are those confined either to the interface, or to one or other of the media. Löwenherz *ibid.* 1894, **15**, 389) interpreted the hydrolysis of an ester partly miscible in water and present in excess as saponification occurring in the aqueous phase only. The rate of hydrolysis is increased by adding acid catalysts. The reaction rate is then

$$-\frac{dx}{dt} = k C_{\text{ester}} C_{\text{acid}}$$

By stirring, the equilibrium solubility of ester in water is maintained and so  $C_{\text{ester}}$  and  $a$  both remain constant. Thus the rate of hydrolysis is constant. Using alkali as catalyst the reaction equation is approximately, under otherwise identical conditions,

$$-\frac{dx}{dt} = k C_{\text{alkali}}$$

The velocity equations of soap and fatty acid manufacture are subject of these equations.

The studies have been extended to the hydrolysis of an ester distributed between two liquid phases, aqueous acid solution (where reaction occurred) and benzene (Goldschmidt and Messerschmitt, *ibid.* 1899, **31**, 235). If it is assumed that the distribution equilibrium is maintained (during the reaction, the reaction equation is:

$$-\frac{dx}{dt} = k \frac{V_1 a}{V_2 + V_1 a} (a - x)$$

where  $V_1$  denotes the volume of the aqueous layer and  $V_2$  that of the benzene layer;  $a$  is the absolute amount of ester and  $x$  is the amount hydrolysed at time  $t$ ;  $k$  is the velocity constant and  $\alpha$  is the distribution constant =  $\frac{C(\text{in water})}{C(\text{in benzene})}$ .

Integration gives

$$k = \frac{1}{t} \frac{V_2 + V_1 a}{V_1 a} \ln \frac{a}{a - x}$$

an equation admirably obeyed when ethyl acetate, distributed between water and benzene, was hydrolysed by water 1.0305N with respect to HCl, and when allowance was made for the fact that an esterification-hydrolysis equilibrium is set up. The analogous reaction using aqueous alkali and benzene obeys the law

$$k = \frac{1}{t} \frac{a + 1}{a} \frac{x}{a(a - x)}$$

when  $V_2$  and  $V_1$  are made equal, and the concentration of alkali and ester are equal; but the reaction follows the equation

$$k = \frac{1}{t} \frac{a + 1}{a} \frac{1}{(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

when the initial concentrations  $a$  and  $b$  are different.

Hydrolysis of a fat by a Twitchell reagent may occur at the interface itself. The hydrophilic

sulphonic acid group dissolves in water; the hydrophobic hydrocarbon groups dissolve in the oil. The reagent therefore is adsorbed at the interface, lowering the surface tension and assisting emulsification as well as bringing oil and water into more intimate contact through the adsorption layer. In Table XIV are given the hydrolytic cleavage efficiencies of 1% sulphonic acid solutions on neutral cotton seed oil heated in a current of steam.

TABLE XIV.—REACTION RATES WITH DIFFERENT TWITCHELL REAGENTS.<sup>1</sup>

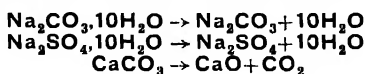
Sulphonic-stearo aromatic com- pound of	Relative amounts of hydrolysis after					
	6½ hrs.	13 hrs.	19½ hrs.	26 hrs.	32½ hrs.	30 hrs.
Naphthalene .	146.7	190.7	201.4	211.4	—	—
Anthracene .	2.5	21.8	76.3	170.7	180.5	190.7
Phenanthrene .	45.7	125.7	177.7	183.6	194.1	201.2

<sup>1</sup> After Lewkowitsch, "Chemical Technology of Oils, Fats and Waxes," 6th ed., 1921, Vol. I, p. 90.

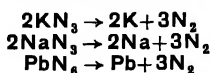
#### E. REACTIONS AT THE SOLID-SOLID INTERFACE.

Adequate discussion of reactions involving the solid-solid interface is impossible in this article. The processes of precipitation-hardening, photography, diffusion in solid media and across phase-boundaries, reactions in certain explosives, and of tarnishing and oxidation of metallic surfaces, and the dissociation of hydrates may be taken as typical of the chemistry of solid two-phase systems (surveyed in Discussion on "Chemical Reactions Involving Solids," Trans. Faraday Soc. 1938, **34**, pp. 821-984).

(i) **Reactions of a Gas at the Solid-Solid Interface.**—A common reaction of this type is found in hydrate and ammoniate formation, and in dissociation of carbonates:



Such reactions do not occur save at the interface between the two solid phases, and it is frequently necessary to scratch or break the crystal before the reaction becomes appreciable. The reaction rate is then autocatalytic, being divided into a slow initiation of reactive centres (the induction period), a spreading of reaction at rapidly growing interfaces, and finally, an exhaustion of the supply of material. Fig. 4 shows a typical curve for the decomposition of azides (Garner, Trans. Faraday Soc. 1938, **34**, 985; Garner and Maggs, Proc. Roy. Soc. 1939, A, 172, 299; Wischin, *ibid.*, p. 314):



Quantitative studies of azide decomposition have shown that metallic nuclei form on the surface and interior of the crystal, and gradually increase in number. The dimensions of each reaction-nucleus also increase steadily;

barium azide the radius  $r$  increased at a constant rate for any given nucleus:

$$\frac{dr}{dt} = A.$$

The constant  $A$  was an exponential function of temperature:  $A = A_0 e^{-\frac{23,000}{RT}}$ . The number  $n$  of nuclei increased according to the expression  $n = Bt^3$ . To interpret the azide reactions, Mott (*ibid.* 1939, A, 172, 325) assumed that nitrogen driven off from the surface releases interstitial atoms of alkali which diffuse into the crystal. These, when their concentration is high enough, aggregate into metallic nuclei. The nuclei then act independently as reaction centres. Aggregation of a similar kind may occur in silver halide crystals during the photographic process. The light liberates numbers of silver atoms (and equivalent chlorine atoms) in proportion to its intensity. Some of the chlorine atoms diffuse away and react with gelatin. The interstitial silver remains, in a pattern of density reproducing the original image, as atomic

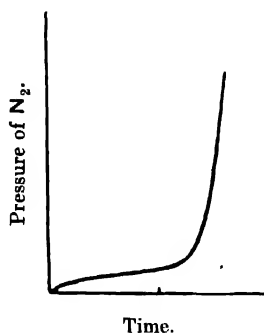
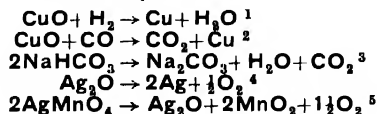


FIG. 4.—INCREASE OF NITROGEN PRESSURE AS A FUNCTION OF TIME IN THE DECOMPOSITION OF AZIDES.\*

centres from which reduction spreads during the developing of the visible picture from the latent image. This reaction is, however, complicated by other factors which are not considered here. (See Discussion on "Chemical Reactions Involving Solids," Pt. IIa, Trans. Faraday Soc. 1938, **34**, 883).

Typical autocatalytic reactions in which the reaction curve resembles that of Fig. 4, although, of course, the atomic and molecular mechanisms may differ *inter se*, are given below:



\* After Mott, Rep. on Prog. Phys. 1939, **6**, 201.

<sup>1</sup> Pease and Taylor, J. Amer. Chem. Soc. 1921, **43**, 2179.

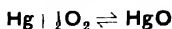
<sup>2</sup> Jones and Taylor, J. Physical Chem. 1923, **27**, 623.

<sup>3</sup> Lescoeux, Ann. Chim. Phys. 1892, [vi], **25**, 430.

<sup>4</sup> Kendall and Fuchs, J. Amer. Chem. Soc. 1921, **43**, 2017.

<sup>5</sup> Sieverts and Theberath, Z. physikal. Chem. 1922, **100**, 463.

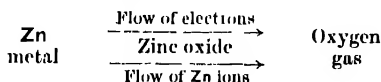
In some cases the deliberate creation of interfaces causes an acceleration in the reaction (Hulett and G. Taylor, *J. Physical Chem.* 1913, **17**, 567). Thus, at 500°C. mercuric oxide gives oxygen and mercury. Because the mercury is a vapour at this temperature, the new interface is not developed and the equilibrium



is only very slowly established. But if iron oxide, manganese dioxide or platinum is added, equilibrium is at once set up. Similar observations were made when silver oxide, mercuric oxide and barium peroxide were decomposed in the presence of other oxides.

(ii) **Tarnishing Reactions.**—The oxidation of metals causes the formation of a skin of oxide which sometimes remains compact and coherent. A new phase is thus created and reaction can continue either at the gas-solid interface by transport of metal atoms or ions through oxide or at the solid-solid interface by a similar transport of oxygen atoms or ions. (For a survey, see Wagner, *Trans. Faraday Soc.* 1938, **34**, 851; Mott, *Rep. on Prog. Phys.* 1939, **6**, 186.) There thus occur simultaneous diffusion and reaction, either of which may limit the rate of growth of the oxide film. Sometimes the film continues to grow steadily (ZnO on Zn) and sometimes oxidation virtually ceases when the film is not a great many atomic layers in thickness ( $\text{Al}_2\text{O}_3$  on Al). (*v.* Vol. III, 368b).

Zinc oxide can take up a stoicheiometric excess of zinc. Oxidation of this metal therefore occurs by diffusion of excess zinc from the metal through the zinc oxide to the external surface, where it reacts with oxygen and forms more oxide. Zinc diffuses slowly, as ions, and electrical neutrality is maintained by an equivalent flow of electrons:



Oxidation of this kind obeys approximately the so-called parabolic diffusion law,  $x^2=kt$  as required by the laws of diffusion (Wagner and Grunewald, *Z. physikal. Chem.* 1938, **B**, **40**, 455. Vernon, Akeroyd and Stroud, *J. Inst. Metals*, 1939, **65**, 301, noted departures from the parabolic diffusion law).

Cuprous oxide is formed on metallic copper by another variation of the diffusion process (*cf.* Wilkins and Rideal, *Proc. Roy. Soc.* 1930, **A**, **128**, 394). Cuprous oxide is capable of taking up a stoicheiometric excess of oxygen (*cf.* Wagner, *Trans. Faraday Soc.* 1938, **34**, 864). The process involves formation of equal numbers of holes at certain  $\text{Cu}^+$  ion lattice sites and  $\text{Cu}^{++}$  ions at others. The lattice is not otherwise disturbed and the crystal may then be regarded as a solid solution of cupric oxide in cuprous oxide. The holes diffuse from the oxide-oxygen interface to the metal-oxide interface, and are there filled by  $\text{Cu}^+$  ions from the metal, the electron liberated passing into the oxide lattice and converting an equivalent number of  $\text{Cu}^{++}$  ions into  $\text{Cu}^+$  ions. The mixed oxide near the oxygen-

oxide interface is thus richer in cupric oxide than parts of the film adjacent to the metal.

Sometimes coherent films may be formed which do not grow in thickness beyond a certain value. Thus in the system  $\text{Al}/\text{Al}_2\text{O}_3/\text{O}_2$ , the thickness of the  $\text{Al}_2\text{O}_3$ , if it remains coherent, does not exceed about  $10^{-6}$  cm. An explanation has been given (Mott, *ibid.* 1939, **35**, 1175) in terms of the quantum-mechanical effect known as tunnelling (p. 214c). The tunnelling particle is here the electron, and it has been shown that though the electron might penetrate an oxide layer  $5 \times 10^{-6}$  cm. thick (producing on the external surface of the oxide oxygen ions equivalent to the  $\text{Al}^{++}$  ions which diffuse through the oxide from the metal), these electrons cannot be transmitted through appreciably thicker layers. Layer growth therefore quickly

## F. REFERENCES TO TYPES OF HETEROGENEOUS REACTIONS NOT DESCRIBED ABOVE.

- I. Precipitation-hardening in metals: Taylor and Mott (*Rep. on Prog. Phys.* 1939, **6**, 205); R. Becker (*Ann. Physik.* 1938, [v], **32**, 128).
- II. Development of the photographic image: R. Gurney and N. Mott (*Proc. Roy. Soc.* 1938, **A**, **169**, 151; various papers in the Faraday Society Discussion on "Chemical Reactions Involving Solids" (*Trans. Faraday Soc.* 1938, **34**, pp. 821-984).
- III. Quantitative aspects of crystallisation, of melts, and from aqueous solutions: Taylor's "Treatise on Physical Chemistry," 2nd ed., Vol. II, pp. 1033 *et seq.* (Macmillan & Co.).
- IV. Quantitative aspects of diffusion in solids: Barrer, "Diffusion in and through Solids" (Cambridge Univ. Press, 1941).

R. M. B.

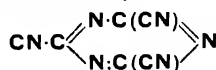
"**HETOCRESOL.**" The cinnamoyl ester of *m*-cresol used as a non-irritant dusting powder in the treatment of tuberculosis.

**HEWETTITE.** A hydrated vanadate of calcium,  $\text{CaO} \cdot 3\text{V}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ , crystallised in the orthorhombic system. It forms mahogany-red, earthy masses, composed of minute silky needles, and occurs somewhat abundantly as an oxidation product of patronite at Minasragra, near Cerro de Pasco in Peru. The mineral fuses readily to a dark-red liquid, and is slightly soluble in water. Sp.gr. 2.55.

*Metahewettite* is identical with hewettite in composition and in crystallising in the orthorhombic system, but it differs somewhat in its optical characters and behaviour during dehydration. It is found as a dark-red, powdery impregnation in sandstone at Paradox Valley in Colorado, and over a wide area in eastern Utah.

L. J. S.

## HEXACYANOGEN,



is produced by dehydrating the triamide of cyanuric acid at 210-250° with phosphorus pentoxide (Ott, *Ber.* 1919, **52**, [B], 661). M.p. 119°, b.p. 262°/771 mm., 119°/0.5 mm. It is decomposed by water and alcohols but withstands the action of dry hydrogen chloride.



• **n-HEXADECANEDICARBOXYLIC ACID**,  $\text{CO}_2\text{H}[\text{CH}_2]_{14}\text{CO}_2\text{H}$ , is prepared by what is essentially the method of Crum-Brown and Walker (Annalen, 1891, 261, 125), i.e. by electrolysis of potassium ethyl sebacate followed by hydrolysis of the resulting ethyl hexadecanedicarboxylate (A. Franke and O. Liebermann, Monatsh. 1923, 43, 589). It has also been obtained by indirect reduction of clupanodonic acid (Y. Inoue and H. Kato, Proc. Imp. Acad. Tokyo, 1934, 10, 463).

Hexadecanedicarboxylic acid has m.p.  $124^\circ$ . For absorption spectrum, see Ramart-Lucas and F. Salmon-Legagneur (Compt. rend. 1929, 189, 915); for crystallography, W. A. Caspari (J.C.S. 1928, 3235); for X-ray measurements, A. Normand, J. Ross and E. Henderson (J.C.S. 1926, 2632); and for dipole moment, C. Smyth and W. Walls (J. Amer. Chem. Soc. 1931, 53, 527).

This acid has achieved some technical importance by reason of its conversion into cycloheptadecanone by heating its salts of rare earths (Swiss P. 122510-3; L. Ruzicka and co-workers, Helv. Chim. Acta, 1926, 9, 230, 389). W. Carothers and J. Hill (J. Amer. Chem. Soc. 1933, 55, 5043) have utilised the thallium salts (the first product of heat treatment being linear polymer) and have also obtained polymeric cyclic esters on heating the acid with trimethylene glycol (*ibid.* 1932, 54, 1559). The suitability of several derivatives of hexadecanedicarboxylic acid for this ring-closure has also been examined (P. Pfeiffer and E. Lübke, J. pr. Chem. 1933, [ii], 136, 321; P. Chuit and J. Hauser, Helv. Chim. Acta, 1929, 12, 850; cf. also S. Landa and A. Kejvan, Coll. Czech. Chem. Comm. 1931, 3, 367).

**HEXAHYDRITE** (v. Vol. IV, 321b).

**HEXAHYDROXYBENZENE** is obtained by acidifying potassium carbonyl (Lerch, Annalen, 1862, 124, 22); by reducing tetrahydroxybenzoquinone (Maquenne, Bull. Soc. chim. 1887, [ii], 48, 64; cf. G.P. 368741); and by oxidising inositol with nitric acid (Gelormini and Artz, J. Amer. Chem. Soc. 1930, 52, 2483). It forms needles which darken without melting on heating and is a strong reducing agent. Esters are prepared by fusing it with the anhydride and Na salt of the appropriate acid (Backer and Van der Baan, Rec. trav. chim. 1937, 56, 1161).

**HEXALDEHYDE** (*n-Caproaldehyde*). This aldehyde,  $\text{C}_6\text{H}_{11}\text{CHO}$ , is used in perfumery, and has a fruity odour, by which special effects can be achieved in most floral perfumes. It has b.p.  $131^\circ/760$  mm.,  $28^\circ/12$  mm.;  $d_{20}^{20}$  0.8337.

E. J. I

"**HEXALIN**" (v. Vol. I, 147d).

"**HEXAMECOLL**." A preparation of guaiacol and hexamethylenetetramine, used as a disinfectant dusting powder.

**HEXAMETHYLENETETRAMINE** (v. FORMALDEHYDE, Vol. V, 320b).

**HEXAMETHYLENETRIPEROXIDIAMINE** (v. Vol. IV, 543b).

"**HEXAMINE**" (v. Vol. I, 326a).

VOL. VI.—15

**CYCLOHEXANE** (Hexahydrobenzene; hexamethylene),  $\text{C}_6\text{H}_{12}$ .—A hydrocarbon occurring naturally in the petroleum oil of Rumania, Galicia and the Caucasus. It is produced by the catalytic hydrogenation of benzene with a nickel or noble metal catalyst (Sabatier and Senderens, Compt. rend. 1901, 132, 210; Ipatiew, J. Russ. Phys. Chem. Soc. 1907, 39, 681-693; Amer. Chem. Abstr. 1907, 1, 2878; Skita and Meyer, Ber. 1912, 45, 3593).

Pure cyclohexane has m.p.  $6.4^\circ\text{C}$ ., b.p.  $81^\circ$ ,  $d_{20}^{20}$  0.7791, and  $n_D^{20}$  1.425. The commercial product has a melting-point of about  $+3^\circ$  which indicates a fairly high degree of purity. It is the best known solvent for both paraffin wax and rubber, and is also a valuable solvent for recrystallising purposes, being less toxic than the corresponding unsaturated hydrocarbons cyclohexene and benzene. A summary of observations on the toxicity of these three hydrocarbons is given in E. Browning, "Toxicity of Industrial Organic Solvents," issued by the Medical Research Council (Industrial Health Research Board), 1937, pp. 118-122. For properties and uses of the commercial solvent, see T. H. Durran, "Solvents," 4th ed., London, 1935.

J. W. B.

**HEXANITRODIPHENYLAMINE** (Hexyl) (Vol. IV, 489a).

**HEXANITRODIPHENYL SULPHIDE** (Picryl sulphide) (Vol. IV, 484c).

**HEXANITRODIPHENYLSULPHONE** (Vol. IV, 484d).

**HEXANITROMANNITOL** (Vol. IV, 500d).

**HEXANITROSULPHOBENZIDE** (Vol. IV, 484d).

**CYCLOHEXANOL** (Hexahydrophenol),

$\text{C}_6\text{H}_{11}\text{OH}$ .

This isocyclic alcohol is produced by the catalytic hydrogenation of phenol in either the gaseous or the liquid phase. Conditions for this hydrogenation have been described in various publications and patents (Sabatier and Senderens, Compt. rend. 1903, 137, 1025; Ipatiew, Ber. 1907, 40, 1286; Brochet, Compt. rend. 1922, 175, 583).

Common to these processes is the need for somewhat raised temperatures although the reaction itself is highly exothermic. Phenol is more readily hydrogenated than its homologues, and this seems to be only partly explained by the greater purity of the crystalline substance. A nickel catalyst is the one most commonly employed. Pure cyclohexanol is a crystalline solid, m.p. ca.  $25^\circ$ , b.p.  $161.5^\circ$ ,  $d_{20}^{20}$  0.947 and  $n_D^{21}$  1.4654. Cyclohexanol is stated to exist in two allotropic modifications (Nagornov, Amer. Chem. Abstr. 1928, 22, 4485). Data as regards the melting-point are therefore somewhat uncertain.

Commercial cyclohexanol has a high degree of purity, containing only a small proportion (under 0.5%) of cyclohexanone. It has been marketed under various trade names, e.g. "Anol," "Hexalin," as well as under its chemical name.

Cyclohexanol and its derivatives have obtained

considerable importance as technical chemicals. The alcohol itself is a good solvent for dyes, waxes and shellac, and has found use in the manufacture of polishes, spirit varnishes and inks as well as in the textile industry. The esters, acetate, phthalate, etc., have found considerable use as solvents and plasticisers.

**Methylcyclohexanol**,  $C_6H_{10}Me.OH$ . While four structurally isomeric methylcyclohexanols exist, interest is mainly centred in the three derivatives of the corresponding *ortho*-, *meta*- and *para*-cresols, i.e. the *hexahydrocresols*. These are obtained from the cresols by catalytic hydrogenation in the presence of a nickel catalyst under varying conditions according to the process used. Common to all is the use of a somewhat raised temperature. The 1:2-, 1:3- and 1:4-methylcyclohexanols show small differences in boiling-point and other physical characteristics (1:2- b.p. 167–168°,  $d^{15.5}_4$  0.933; 1:3- b.p. 175–176°,  $d^{15.5}_4$  0.924; 1:4- b.p. 173–174°,  $d^{15.5}_4$  0.924). Stereoisomeric forms of *m*-methylcyclohexanol are known.

The methylcyclohexanol of commerce (also known under various trade names such as "*Sertol*," "*Methylanol*," "*Methylhexalin*") is a mixture of the above three isomers in various proportions, and may also contain small quantities of cyclohexanol, and usually contains a very small percentage of the corresponding ketones. A typical commercial product has the following approximate composition: *o*-methylcyclohexanol 30%; *m*-methylcyclohexanol 35%; *p*-methylcyclohexanol 35%, and has b.p. 168–175°,  $d^{15.5}_4$  0.925.

Methylcyclohexanol has become a solvent of considerable commercial importance. This is due not only to its solvent power for fats, oils and dyes, but also to its outstanding ability to reduce surface tension and to stabilise emulsions. These properties have led to an extensive use of this solvent in the textile industry, for the preparation of textile- laundry- and dry-cleaning soaps, and for textile dyeing and printing.

The esters, acetate, phthalate, stearate, etc., are used extensively as solvents and plasticisers in various branches of industry (*v. Durran*, "Solvents," 4th ed., 1935).

J. W. B

**HEXATRIENE** (Vol. II, 161a).

**"HEXANON"** (Vol. I, 380d).

**HEXOGEN** (Vol. III, 535d).

**HEXOKINASE** (Vol. V, 24c, 35c).

**HEXOPHAN** (Bayer Products). 2-(4'-hydroxyphenyl) quinoline-4:3'-dicarboxylic acid, used in the treatment of gout (*Pharm. J.* 1925, 114, 202). "*Lytophan*" is 2-phenylquinoline-4:3'-dicarboxylic acid (*Gudzent and Keip, Ther. d. Gegenw.* 1921, 62, 127).

**HEXURONIC ACID** (*v. Vol. I*, 502a).

**HEXYL** (*v. Vol. IV*, 489a).

**n-HEXYL ALCOHOL**,  $C_6H_{13}.OH$ . This alcohol and its esters have been used as synthetic perfumes. They are, however, of little importance.

E. J. P.

**HIBBENITE** *v. HOPEITE*.

**HIDDENITE**. A transparent, emerald-green variety of the mineral spodumene,

$LiAlSi_2O_6$ , used as a gem-stone. It is found with emerald in North Carolina, and has been popularly, but erroneously, known as "lithia-emerald."

L. J. S.

**"HIDUMINIUM"** (*v. Vol. I*, 253b).

**HIERATITE** (*v. Vol. V*, 606).

**HIGHGATE RESIN**. Copalin, a fossil resin resembling copal found in the blue clay of Highgate Hill.

**HIGH PRESSURE REACTIONS**. *The Influence of Pressure upon Chemical Reactions in the Liquid Phase*.—In considering the effect of pressure upon the course and rate of a chemical reaction in the liquid phase it is necessary to take into account its influence upon certain of the physical properties of the medium. Thus, for example, any change in the specific volume, viscosity, specific heat or the melting- and boiling-points of the reactants may exert an appreciable influence upon the velocity. It is also well known that solvents may interfere with the mechanism of a reaction, and in a number of instances a correlation has been observed between the effect of the solvent and such properties as refractive index, dielectric constant and cohesion (*Moelwyn-Hughes, "Kinetics of Reactions in Solution," The Clarendon Press, 1933, p. 51*). Although such relationships are quite specific, it is clear that any factor, such as pressure, tending to bring about a change in one or more of them will exert an influence upon reaction velocity. There is also evidence that pressure may give rise to an induced or increased polarity of the reactant molecules, and it has been suggested that some of the potential energy gained by a system as the result of isothermal compression may, in certain circumstances, become available as part of the activation energy necessary for reaction to take place (*Fawcett and Gibson, J.C.S., 1934, 386*).

Two important properties which require consideration are compressibility and thermal dilatation. The volume change when a liquid is subjected to hydrostatic pressure is determined by changes in molecular configuration, by the closer packing of individual molecules and, to some extent, by the deformation or compression of the molecules themselves.

The thermal dilatation of liquids, in general, decreases with increasing pressure up to about 4,000 atm., after which the pressure effect becomes irregular and, in some instances, changes in sign, the dilatation increasing over a range of several thousand atmospheres and then again decreasing.

It will be seen from the data in Table I that both in respect of the compressibility and the dilatation, there is a tendency for most liquids at high pressures to lose the individual differences which usually characterise them; thus, the ratio of the dilatation of ether to that of amyl alcohol at low pressures is 1.5 whilst at 12,000 kg. per sq. cm. it has fallen to 1.03; furthermore, the effect of pressure in decreasing the compressibility is much greater than its effect in decreasing the dilatation.

*The Collision Number in the Liquid Phase*.—Collisions between molecules in a liquid differ in some important respects from those in a gas.

TABLE I.—CHANGES OF COMPRESSIBILITY AND THERMAL EXPANSION PRODUCED BY PRESSURE (Bridgman, Proc. Amer. Acad. 1913, 49, 1).

Liquid.	Compressibility $K$ .			Dilatation $\delta$ .		
	$K_{12,000}$	$K_{6,000}$	$K_{12,000} \times 10^6$	$\delta_{12,000}$	$\delta_{6,000}$	$\delta_{12,000} \times 10^4$
Methyl alcohol	18.4	2.20	7.4	4.29	1.23	2.98
Ethyl alcohol	13.7	2.02	8.1	45.0	1.30	2.68
<i>n</i> -Propyl alcohol	15.8	1.94	7.0	4.80	1.33	2.37
isoButyl alcohol	16.6	1.68	8.6	4.15	1.17	2.75
isoAmyl alcohol	14.4	1.88	7.4	4.40	1.30	2.40
Ethyl ether	—	1.62	9.6	—	1.32	2.48
Acetone	—	1.85	8.7	—	1.35	2.82
Carbon disulphide	13.8	1.82	8.7	5.47	1.31	2.62
Phosphorus trichloride	14.2	1.81	8.0	4.84	1.31	2.78
Ethyl chloride	—	1.78	9.0	—	1.37	2.67
Ethyl bromide	14.9	1.87	8.2	—	1.33	2.60
Ethyl iodide	14.9	1.89	8.1	4.86	1.22	2.48

In a liquid containing, for example, two reacting species A and B in solution, each reactant molecule will be surrounded by a cage of solvent molecules and collision can only occur by a process of diffusion during which one molecule penetrates into the cage occupied by another. Once having become "co-ordinated" in this way the 2 molecules may make a large number of collisions before separating. In a gas a collision is a unique event and a second collision between any two specific molecules hardly ever occurs immediately.

The number of binary collisions in a gas is given by the equation:

$$1/2 n_1 n_2 \sigma_{1,2}^2 \left\{ 8\pi RT \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \right\}^{\frac{1}{2}} \quad (1)$$

where  $n_1$  and  $n_2$  are the number of molecules per c.c. of molecular weight  $M_1$  and  $M_2$ , respectively, and  $\sigma_{1,2}$  is the average molecular radius. The corresponding number for a liquid under similar conditions would be about  $10^3$  times greater and would increase with pressure approximately as the viscosity. Reaction occurs as the result of collisions between molecules having energies equal to or in excess of a certain critical value  $E$ . The number of such collisions

is obtained by multiplying (1) by  $e^{-\frac{E}{RT}}$ . The majority of liquid phase reactions are bimolecular and the rate of change is given by

$$\frac{dn}{dt} = C n_1 n_2 \sigma_{1,2}^2 \left\{ 8\pi RT \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \right\}^{\frac{1}{2}} e^{-\frac{E}{RT}} \quad (2)$$

where  $C$  is the ratio of the collision number in the liquid phase to that in the gaseous phase.

From (2) the bimolecular velocity constant  $k$ , expressed in litres per g. mol. per sec. can be evaluated. Thus, if  $N$  is the Avogadro number

$$k = \frac{dn}{dT} \frac{1}{n_1 n_2} \frac{N}{1,000} \quad (3)$$

By combining (2) and (3)

$$k = \frac{N}{1,000} C \sigma_{1,2}^2 \left\{ 8\pi RT \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \right\}^{\frac{1}{2}} e^{-\frac{E}{RT}} \quad (4)$$

and, differentiating with respect to temperature,

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad (5)$$

A similar result may be obtained from the Arrhenius equation

$$k = BZ e^{-\frac{E_a}{RT}} \quad (6)$$

In this equation  $Z$  denotes the number of encounters between reacting molecules under specified conditions,  $E_a$  is the "critical increment of energy" and  $B$  is a factor representing the probability that a collision involving the requisite energy will lead to reaction.

On differentiating (6) with respect to temperature

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad (7)$$

From (5) and (7)

$$E = E_a - \frac{1}{2} RT \quad (8)$$

The difference between  $E$  and  $E_a$  is usually unimportant except where  $T$  is high or  $E$  is small.

The velocity constants and critical increments of a large number of bimolecular reactions in solution have been measured at atmospheric pressure and about 40% of them are found to have normal velocities in accordance with (1); in such cases the calculated collision frequency varies little from reaction to reaction, an average value being about  $2.8 \times 10^{11}$ , and the probability factor does not differ much from unity. Of the remaining reactions the greater part are "slow" in the sense that their velocities are from 10 to 100,000 times slower than the calculated values and  $B$  is less than unity, whilst a few, on the same basis, may be classified as "fast,"  $B$  being greater than unity. All three types of reaction show positive responses to pressure.

Whilst the cause of such abnormal rates is not known with certainty there are a number of factors which might be responsible. Thus, in the case of "slow" reactions the endothermic formation of a complex prior to the reaction proper, deactivation by molecules of the solvent, or special conditions of orientation or of internal phase of the reacting molecules at the moment of impact would account for the apparent slowness of the reaction. "Fast" reactions might be due to the exothermic formation of a complex prior to reaction, the distribution of the energy of activation among a number of internal degrees of freedom of the reactant molecules, the occurrence of a chain reaction, or activation by some external source of energy (Moelwyn-Hughes, *op. cit.*).

If it be assumed that, prior to reaction, two molecules possessing the requisite activation energy must come together and form a pre-activated complex, then reaction will occur when the life period  $\theta$  of the complex is equal to or greater than the time  $t$  required for the completion of the internal motions of the molecules necessary to bring the atoms to appropriate distances, and with suitable relative velocities for new bonds to be formed. If the collision complex is stable,  $\theta$  will be large and the factor  $B$  of equation (6) will be constant and independent of  $E$ ; on the other hand, when, *vis* appreciably greater than  $\theta$ , a correlation should be observable between  $BZ$  and  $E$ . Since the life of the complex is terminated, either by separation of its constituents by deactivation in a collision, or by chemical transformation, the effect of hydrostatic pressure would be, presumably, to increase its stability (Fairclough and Hinshelwood, J.C.S. 1937, 538). In this connection recent work has shown that whilst pressure accelerates both "normal" and "slow" reactions its effect upon the latter class is far greater than upon the former; in "slow" reactions moreover both  $B$  and  $E$  are found to vary with pressure in a regular manner.

As a typical example of a normal reaction the interaction of sodium ethoxide and ethyl iodide in alcohol solution may be considered (Gibson, Fawcett and Perrin, Proc. Roy. Soc. 1935, A, 150, 223). The reaction



is bimolecular and the velocity constants are found to vary with the initial concentration of the sodium ethoxide but not with that of the ethyl iodide. In Table II the constants for 0.1 normal solutions at temperatures between 15° and 30°C. and over the pressure range 1–5,000 kg./cm.<sup>2</sup> are given.

TABLE II.—THE VELOCITY CONSTANTS FOR THE INTERACTION OF SODIUM ETHOXIDE AND ETHYL IODIDE IN ALCOHOL SOLUTION AT VARIOUS PRESSURES.

Tem- perature, °C.	Pressure, kg./cm. <sup>2</sup> .	$K_1 \times 10^3$ , g. mol./litre/minute.	$K$ (obs.) $\times 10^3$ .	$K$ (calc.) $\times 10^3$ .
14.85	1	—	2.30	2.27
19.95	1	—	4.19	4.26
25.0	1	—	7.73	7.79
30.0	1	—	13.60	13.90
14.85	2,980	4.25	3.65	3.57
19.95	2,980	7.59	6.53	6.72
25.0	2,980	14.40	12.40	12.30
30.0	2,980	25.20	21.60	22.00
15.0	5,000	5.6	4.6	4.65
20.0	5,000	10.3	8.4	8.48
25.1	5,000	19.4	15.9	15.80
30.1	5,000	34.2	28.1	27.50

The constants  $K_1$  in column 3 of the table are uncorrected for the changes in concentration

due to the thermal expansion and compressibility of the solvent; in column 4,  $K$  (obs.) are the corrected values.

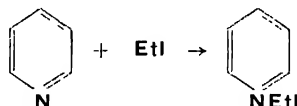
It will be seen that whilst the velocity increases with pressure the effect is not very marked and at 5,000 kg./cm.<sup>2</sup> the rate is only about double that at atmospheric pressure. From the experimentally determined constants the values of  $BZ$  and  $E$  (equation 6) are found to be:

Pressure, kg./cm. <sup>2</sup> .	$BZ \times 10^{13}$	$E$ , g.-cal.
1	1.28	20,740
3,000	2.23	20,800
5,000	1.32	20,340

The values of  $K$  calculated from these constants are given in column 5 of Table II. The changes in  $BZ$  and  $E$  with pressure are not, in this instance, of sufficient magnitude to enable any distinction to be made as to their relative importance in determining the observed acceleration of the reaction.

Somewhat similar results are found for the hydrolysis of sodium monochloroacetate by sodium hydroxide in aqueous solution. The reaction is bimolecular and "normal" and its velocity increases with pressure, the value at 12,000 kg./cm.<sup>2</sup> being about 6.5 times the value at atmospheric pressure.

The above reactions may now be compared with a typical "slow" reaction, namely that between pyridine and ethyl iodide in acetone solution



The rate of this reaction at 3,000 kg./cm.<sup>2</sup> is 7.2 times, and at 8,500 kg./cm.<sup>2</sup> is 47.5 times as great as that at atmospheric pressure. The variations of the constants of the Arrhenius equation with pressure are as follows:

Pressure, kg./cm. <sup>2</sup> .	$BZ \times 10^7$ .	$E$ , g.-cal.
1	2.13	14,390
2,975	71.6	15,350
5,000	197.0	15,510
8,500	2,490.0	16,380

Both constants show a marked increase with pressure.

In the foregoing examples the reaction rates have been measured in dilute solution and are, therefore, influenced to some extent by changes in the physical properties of the solvent with pressure.

An interesting example in which the pure reactants and products only are concerned is that of the esterification of acetic acid by a series of alcohols (P'eng, Sapiro, Linstead and Newitt, J.C.S. 1938, 784). Measurements have been made of the rates of esterification at a number of pressures from atmospheric to 4,000 atm. and the corresponding velocity constants have been determined. The values of the

constants of the Arrhenius equation for the reactions are given below :

VALUES OF THE CONSTANTS OF THE ARRHENIUS EQUATION FOR THE RATE OF ESTERIFICATION OF ACETIC ACID WITH A SERIES OF ALCOHOLS.

Alcohol.	Pressure, atm.	E, g.-cal.	A or BZ.
Ethyl . . . .	1	13,770	$4.58 \times 10^3$
	2,000	13,790	$2.40 \times 10^3$
	3,000	13,830	$6.10 \times 10^3$
	4,000	13,980	$1.61 \times 10^4$
<i>n</i> -Propyl . . . .	1	13,550	$4.10 \times 10^3$
	2,000	13,910	$2.98 \times 10^3$
	3,000	14,190	$8.87 \times 10^3$
	3,750	14,740	$3.33 \times 10^4$
<i>n</i> -Butyl . . . .	1	13,720	$5.69 \times 10^3$
	2,000	14,580	$7.00 \times 10^3$
	3,000	14,950	$2.44 \times 10^4$
	3,750	15,190	$5.72 \times 10^4$
<i>iso</i> Propyl . . . .	1	15,890	$3.20 \times 10^3$
	2,000	19,400	$2.15 \times 10^6$
	3,000	20,660	$2.66 \times 10^7$
	3,750	22,220	$4.38 \times 10^8$
<i>iso</i> Butyl . . . .	1	16,480	$4.84 \times 10^4$
	2,000	17,850	$1.30 \times 10^6$
	3,000	18,240	$3.35 \times 10^6$
	3,750	18,780	$1.16 \times 10^7$
<i>sec.</i> -Butyl . . . .	1	17,460	$2.50 \times 10^4$
	2,000	19,790	$3.53 \times 10^6$
	3,000	21,010	$4.90 \times 10^7$
	3,750	21,720	$2.22 \times 10^8$

Both *E* and BZ increase with pressure, the effect being greatest with *isopropyl* and *sec.*-butyl alcohols; there is also, in all cases, a functional relationship between the two constants, straight lines being obtained by plotting values of *E* against log BZ.

*Unimolecular Decompositions.*—It would be expected from the Le Chatelier-Braun principle of mobile equilibrium that increase of pressure

would exert a retarding effect upon the rate of a unimolecular reaction, and such is found to be the case. Phenylbenzylmethylallylammonium bromide decomposes at a measurable rate in chloroform solution at temperatures between 25 and 45°C. The reaction is reversible and to determine the velocity constant of the decomposition it is necessary to measure the equilibrium constants  $\alpha$  at the various temperatures employed. The results for a 0.0975 normal solution are summarised in Table III (Williams, Perrin and Gibson, Proc. Roy. Soc. 1936, A, 154, 684).

TABLE III.—DECOMPOSITION OF PHENYL-BENZYLMETHYLLALLYLAMMONIUM BROMIDE IN CHLOROFORM SOLUTION.

(Strength of solution = 0.0975 normal)

Temperature, °C.	Pressure, kg./cm. <sup>2</sup> .	$\alpha$	$K$ (obs.) $\times 10^4$ .	$K$ (calc.) $\times 10^4$ .	$\alpha K$ $\times 10^4$ .
g. mol./litre/minute.					
25.0	1	7.97	3.23	3.16	0.258
29.05	1	5.1	7.4	7.1	0.377
34.95	1	2.21	15.8	15.85	0.350
39.0	1	1.44	34.3	34.7	0.403
44.9	1	0.64	74.5	73.0	0.478
25.0	2,080	75.5	2.16	2.24	1.63
29.05	2,080	34.0	5.1	4.6	1.74
34.95	2,080	16.8	10.7	10.0	1.80
40.0	2,080	10.6	22.0	28.4	2.43
44.9	2,080	7.37	47.6	48.9	3.51

*Polymerisations by Pressure.*—As an example of the effect of pressure upon this class of reaction the behaviour of  $\alpha$ -methylstyrene may be given. Under normal conditions the trimeride is the highest polymer obtained either by heat alone, or with addition of Florida earth or boron trichloride; on the other hand, at 5,000 atms. and 100°C., a mixture of high polymers with a mean molecular weight of 5,600 is obtained. The effects of temperature and time upon the yields obtained at different pressures are as follows:

POLYMERISATION OF  $\alpha$ -METHYLSTYRENE (Sapiro, Linstead and Newitt, J.C.S. 1937, 1784).

Temperature, °C.	Pressure, atm.	Time, hours.	Yield, per cent.			Mean molecular weight of high polymers.
			Monomer.	Low polymers.	High polymers.	
100	5,000	1	98-99	—	—	—
		14	32.6	3.4	64.0	—
		96	15	—	85	5,400-5,800
110	3,500	95	23	12	65	2,600
		96	68.3	27.2	4.5	1,600
125	4,000	260	46.0	48.7	5.3	—
		96	46.4	27.7	26.0	1,050
150	10,000	47	21.0	81.9 (M.W. = 370.)	79.0	1,170
		48			none	—

Another example of pressure polymerisation has been worked out in detail (Raistrick, Sapiro and Newitt, J.C.S. 1939, 1761). When *cyclo-*

pentadiene in the pure liquid phase is subjected to high hydrostatic pressure, reaction is found to proceed in three distinct stages, depending

upon the temperature and pressure, viz. (1) dimerisation to dicyclopentadiene only, (2) association to higher polymers amongst which the trimer and tetramer have been identified, and (3) a violent disruptive reaction producing methane and a highly carbonised residue.

The bimolecular velocity constants of the dimerisation reaction have been measured over the temperature range 0–40°C. up to a pressure of 5,000 atm. The values of the ratio  $K_p/K_1$  tabulated below show an increase with temperature, particularly in the higher pressure ranges.

THE INFLUENCE OF TEMPERATURE UPON THE RATIO  $K_p/K_1$  FOR VARIOUS PRESSURE RANGES.

Values of  $K_p/K_1$  for the pressure range (atm.):

Temp., °C.	1–500.	1–2,000.	1–3,000.	1–4,000.	1–5,000.
0°	1.53	5.48	12.3	23.7	44.2
20°	1.66	7.05	15.5	33.3	—
30°	1.86	7.74	18.5	—	—
40°	2.05	8.75	—	—	—

As with most other liquid phase reactions which have been investigated at high pressures the values of BZ and  $E$  of the Arrhenius equation increase with pressure. The term BZ is made up of the collision number  $Z$  and a probability factor  $B$  both of which may vary with pressure. If the collision number be assumed to remain constant at  $10^{14}$ , i.e. about  $10^3$  times greater than the gas collision number, then it is found that for a pressure increase of 5,000 atm. the probability of interaction between two cyclopentadiene molecules with the requisite energy  $E$  is increased by more than  $10^3$  times. This result is not improbable; the viscosity of the medium is increased by a factor of at least 10 at the higher pressure, and the tendency towards orientation of the molecules, always evident in the liquid phase, is thereby increased. If such orientation brings pairs of molecules into the correct relative position for interaction, the probability factor will show a corresponding increase.

The activation energy term  $E$  is composite and made up of energy contributions arising from changes in the physical properties of the medium and from variations of the rate of diffusion of the reactant molecules. Since BZ also contains terms which depend upon such changes some simple relationship between them is to be expected. In nearly all cases it is found that on plotting  $\log BZ$  against  $E$  a straight line is obtained. It has also been shown by Newitt and Wassermann (J.C.S. 1940, 735) that the parameters  $E$  and BZ calculated for constant volume conditions are independent of pressure.

D. M. N.

**HIGH TEMPERATURE CARBONISATION** (v. Vol. V, 367b, 450, 451).

**HIROGANE**.—"Hiiroganē" is the name given to a blood-red coloured metallic coating

obtained on copper by treatment with an aqueous solution of copper sulphate and verdigris, or on copper alloys by heating with a paste containing a cupric salt, borax and a little water. The colour may be due to a mixture of cuprous and cupric oxides (cf. Miyazawa, J. Chem. Ind. Tokyo, 1917, 20, 1102; J.S.C.I. 1918, 37, 211a).

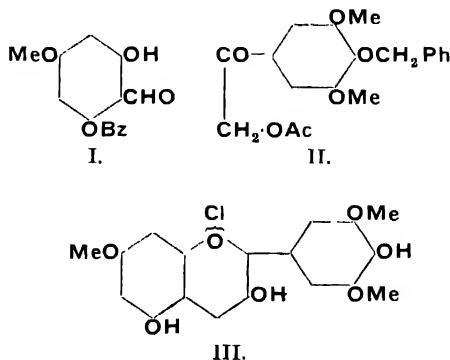
**HILGARDITE**. Hydrated chloroborate of calcium,  $\text{Ca}_3(\text{B}_6\text{O}_{11})_2\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ , as colourless triangular plates with monoclinic-domatic symmetry. It is found amongst the sandy residue accumulating at the bottom of the brine well in the Choctaw salt dome in Louisiana. Dimorphous with this, and with the crystals intergrown in parallel position, is *parahilgardite* with triclinic-pedial symmetry (C. S. Hurlbut and R. E. Taylor, Amer. Min. 1937, 22, 1052; 1938, 23, 765, 898).

L. J. S.

**HINK'S TEST** (v. Vol. II, 167a).

**HIPPOCASTANIN** (v. Vol. III, 27b).

**HIRSUTIDIN** is the anthocyanidin obtained by acid-hydrolysis of hirsutin (q.v.), a colouring matter of the petals of *Primula hirsuta*. Karrer and Widmer (Helv. Chim. Acta, 1927, 10, 758) recognised it as the 5:3':5' or 7:3':5'-trimethyl ether of delphinidin (q.v.) from analytical data, colour reactions and the formation of syringic acid when hirsutone (see HIRSUTIN) was hydrolysed by means of alkali. The correctness of the second alternative was established by synthesis (Bradley, Robinson and Schwarzenbach, J.C.S. 1930, 794). 4-O-Methyl-2-O-benzoylphloroglucinaldehyde (I) and  $\omega$ -acetoxy - 4 - benzyloxy - 3:5 - dimethoxyacetophenone (II) condensed by means of dry HCl in ethyl acetate solution gave a benzoylated salt, from which (III), identical with hirsutidin chloride, was obtained by de-acylation.



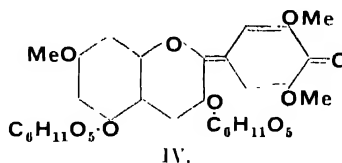
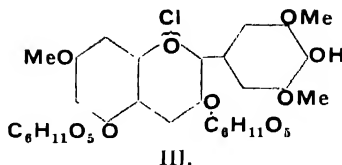
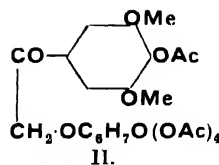
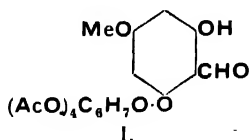
The chloride,  $\text{C}_{18}\text{H}_{17}\text{O}_7\text{Cl}$ , crystallises from aqueous HCl in the form of short, dark red, pointed prisms. It dissolves in hot water to a pale red solution with a violet tinge, but this rapidly becomes colourless on boiling owing to formation of the *pseudo-base*; on adding acid the colour is restored. Even in hot 0.5% HCl the salt is only sparingly soluble to a reddish solution, and a cold saturated solution in 4% HCl is pink. A freshly prepared

solution in methyl alcohol is violet-red, and this becomes pure blue on the addition of solid sodium acetate or sodium carbonate solution. If the solution is kept for some time previous to the test a greenish-blue colour is obtained. The chloride dissolves in 0.1N aqueous sodium hydroxide forming a purple-blue solution which rapidly becomes crimson-blue (dichroic) and then fades to emerald green. The cooled solution in hot 0.25% HCl apparently contains much *pseudo-base* since excess of sodium carbonate gives a brownish-green solution changing to olive-green. Unlike cyanidin and delphinidin (*q.v.*), both of which reduce Fehling's solution in the cold, hirsutidin is affected only on heating. It gives no colour reaction with ferric chloride.

W. R.

**HIRSUTIN.** A study of the colouring matters of *Primula* has shown that the petals of *P. viscosa* owe their hue to malvin, which is also present in the blue wild mallow (*Malva sylvestris*), that *P. integrifolia* contains malvin and an anthocyanin with a smaller methoxyl-content, whilst *P. hirsuta* contains hirsutin, a methyl ether of malvin (Karrer and Widmer, Helv. Chim. Acta, 1927, 10, 758). Hirsutin chloride crystallises readily and separates from hot 1% HCl on adding 5% methyl-alcoholic HCl in the form of deep brownish-violet felted needles of the *tetrahydrate*,  $C_{30}H_{37}O_{17}Cl \cdot 4H_2O$  (dried in a desiccator over sulphuric acid), m.p. 150–153° (decomposing after sintering at about 145°). The anthocyanin is sparingly soluble even in very dilute HCl to a violet-red solution which is bluer than that of cyanin (*q.v.*). In alcohol the colour is a deeper blue. When sodium acetate or sodium carbonate is added to an acid solution the violet colour-base (IV) separates; hirsutin is unique amongst natural anthocyanins in that the colour-base does not dissolve in alkalis to form a blue alkali salt. Hirsutin is hydrolysed on heating with 20% HCl to hirsutidin (1 mol.) (*q.v.*) and glucose (2 mol.). It is oxidised by 15% hydrogen peroxide to *hirsutone*,  $C_{30}H_{39}O_{19}$ , a colourless, highly crystalline ketone which dissolves easily in hot water but sparingly in cold. Hirsutone is very easily hydrolysed by means of aqueous sodium hydroxide with formation of syringic acid (3:5-di-O-methylgallic acid).

The constitution of hirsutin has been established by R. Robinson and co-workers (J.C.S. 1930, 793) who showed that hirsutidin is the 7:3':5'-trimethyl ether of delphinidin. Robinson and Todd (*ibid.* 1932, 2293) showed that the sugar component is present in the form of two glucose units attached to positions 3 and 5, they synthesised hirsutin by condensing 2-O-tetra-acetyl- $\beta$ -glucosidyl-4-O-methylphloroglucinaldehyde (I) with  $\omega$ -O tetra-acetyl- $\beta$ -glucosidoxy-4-acetoxy-3:5-dimethoxyacetophenone (II) to a flavylum salt which was then deacetylated to hirsutin (III).



Both hirsutidin-3- $\beta$ -glucoside and hirsutidin-5- $\beta$ -lactoside differ in properties from hirsutin. The 3:5-diglucoside structure relates hirsutin to pelargonin, cyanin, paonin, delphin and malvin.

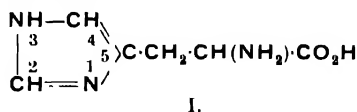
W. B.

**HIRUDIN** (*n.* Vol. 11, 24c).

**HISPIDOGENIN** (*v.* Vol. 11, 385d).

**HISTAMINE** (*v.* Vol. IV, 331d).

**HISTIDINE**, *glyoxaline-5-alanine*,  $\beta$ -*iminazolyt-a-aminopropionic acid*,

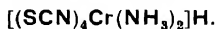


was discovered by Kossel (Z. physiol. Chem. 1896, 22, 176) among the products of hydrolysis of the protamine sturine, which contain 12.9% histidine (Kossel, *ibid.* 1900, 31, 207). It is an important constituent of many animal and vegetable proteins and according to Boone (Med. Bull. Univ. Cincinnati, 1931, 6, 193) it occupies a terminal position, since 5–20% of the histidine content can be isolated in an optically active state after mild alkaline hydrolysis of haemoglobin, edestin, casein and Witte's peptone. Histidine occurs in histones (basic proteins) (Lawroff, Z. physiol. Chem. 1899, 28, 388; Abderhalden and Rona, *ibid.* 1904, 41, 278; Kossel and Staudt, *ibid.* 1926, 159, 172); in gelatin and egg albumin (Simms, J. Gen. Physiol. 1928, 11, 613); in crystalline insulin (2.57%) (Jensen, Wintersteiner and Du Vigneaud, J. Pharm. Exp. Ther. 1928, 32, 387); in horse haemoglobin (7.64%) (Vickery and Leavenworth, J. Biol. Chem. 1928, 79, 377); in crystalline oxyhaemoglobin (7.5–7.6%) (Abderhalden, Fleischmann and Irion, Fermentforsch. 1929, 10, 446); in the antipeptone obtained by pancreatic digestion of fibrin (Kutscher, Z. physiol. Chem. 1898, 25, 195); and has been isolated from other proteins (Hedin, *ibid.* 1896,

22, 191); from red blood corpuscles (15 g. of the hydrochloride from 500 c.c. of blood corpuscle paste) (Jones, *J. Biol. Chem.* 1918, **33**, 429; Hanke and Koessler, *ibid.* 1920, **43**, 521; Chemnitz, *Pharm. Zentralk.* 1928, **69**, 471); from fresh fish (Suzuki, *J. Agric. Tokyo*, 1912, **51**, 1); from fish sperm (Yamagawa, Mikawa and Tomiyama, *J. Imp. Fish Inst. Tokyo*, 1926, **22**, No. 2, 30; *Biol. Abstr.* 1927, **2**, 975); from *Octopus octopodia* (Morizawa, *Acta Schol. Med. Univ. Imp. Kyoto*, 1927, **9**, 299); from diphtheria bacillus (Tamura, *Z. physiol. Chem.* 1914, **89**, 295); from newly hatched chicks (0.05%) (Yoshimura, *J. Chem. Soc. Japan*, 1936, **57**, 318); from the yolk, white, embryo and shell membrane of hen eggs (Calvery, *J. Biol. Chem.* 1932, **95**, 297), and from human hair (0.5%) (Vickery and Leavenworth, *ibid.* 1929, **83**, 523). Histidine occurs in human pregnancy urine and its presence has been suggested as a test for this condition (Foldes, *Biochem. Z.* 1936, **283**, 199; 1936, **285**, 294, 296; cf. Kapeller-Adler, *ibid.* 1936, **285**, 123; Armstrong and Walker, *Biochem. Z.* 1932, **26**, 143; Kapeller-Adler and Haas, *Biochem. Z.* 1935, **280**, 232; Renton, *S. African Med. J.* 1935, **9**, 441; Bodó, *Amer. Chem. Abstr.* 1935, **29**, 1865), but this suggestion has met with severe criticism (Louros, *Klin. Woch.* 1934, **13**, 1156; Gertler, *Endokrinologie*, 1936, **17**, 45; Bosman, *S. African Med. J.* 1935, **9**, 514; Hecksteden, *Deut. Z. ges. gerichtl. Med.* 1935, **24**, 253), especially since it occurs in normal urine (Wada, *Acta Schol. Med. Univ. Imp. Kyoto*, 1930, **13**, 187; Pellizzari, *Boll. Soc. Ital. Biol. sperim.* 1934, **9**, 517). Histidine occurs also in the products of hydrolysis of vegetable proteins, notably in the seeds and seedlings of *Picea excelsa* Linn., *Pinus sylvestris* Linn., *Cucurbita pepo* Linn., *Lupinus luteus* Linn. and *Psium sativum* Linn.; in the case of the conifer seeds 300 g. of dry protein yield 3 g. of histidine hydrochloride (Schulze and Winterstein, *Z. physiol. Chem.* 1899, **28**, 459, 465; 1901, **33**, 547). It is present in *Secale cornutum* (Fränkel and Rainer, *Biochem. Z.* 1911, **74**, 167); in some of the lower fungi (Sullivan, *Science*, 1913, **38**, 678; Reed, *J. Biol. Chem.* 1914, **19**, 260); in soya bean (0.62 g. as dichloride from 5 kg.; Sasaki, *J. Agric. Chem. Soc. Japan*, 1932, **8**, 417) and various species of beans and peas (Kiesel, Belozerskii and Skvorzov, *Zhurnal eksptl. Biol. Med.* 1927, **4**, 538; *Amer. Chem. Abstr.* 1928, **22**, 603; Jodidi, *J. Amer. Chem. Soc.* 1935, **57**, 1142); in potatoes (Yoshimura, *Biochem. Z.* 1934, **274**, 408); and in extracts of ergot (Trabucchi, *Boll. Soc. Ital. Biol. sperim.* 1934, **9**, 501). It is also found in soils (Schreiner and Shorey, *J. Biol. Chem.* 1910, **8**, 381; Skinner, *Bied. Zentr.* 1913, **42**, 213, from Proc. 8th Int. Cong. Appl. Chem. 1912; Lathrop, *Chem. Zentr.* 1917, **II**, 560).

The preparation of histidine usually involves its isolation from the products of protein hydrolysis, and methods by which this is effected can be seen from the following examples. Vickery and Leavenworth (*J. Biol. Chem.* 1928, **78**, 627), and also Mendel and Vickery (*Carnegie Inst. Washington Yearbook*, 1929, **28**, 307) hydrolyse hæmoglobin and then precipitate the silver-histidine compound at  $p_H$  7.0 or 7.4.

After removal of the silver, the histidine is separated from most of the accompanying amino-acids by precipitation with mercuric sulphate (Hopkin's reagent) and recovered by treatment with hydrogen sulphide. The histidine is crystallised at the isoelectric point and further purified by crystallisation of the dihydrochloride. The base may be conveniently recovered by neutralisation to  $p_H$  7.2 with magnesium oxide, advantage being taken of the solubility of magnesium chloride in alcohol. Smorodincev described the hydrolysis of ox blood with concentrated hydrochloric acid. The excess acid was evaporated, the solution was made slightly alkaline, boiled to drive off ammonia and precipitated with mercuric chloride; the precipitate was dissolved in hydrochloric acid and reprecipitated with mercuric chloride and sodium carbonate, then decomposed with hydrogen sulphide and filtered. Evaporation of the filtrate gave the histidine hydrochloride (43 g. from 1 kg. of dry blood) (*Biochem. Z.* 1930, **222**, 425). The mercuric chloride method is more direct, less costly and gives a better yield than the silver oxide method (Abderhalden *et al.* *Amer. Chem. Abstr.* 1929, **23**, 2994). In the treatment according to Kapfhammer and Sporer (*Z. physiol. Chem.* 1928, **173**, 245) of protein hydrolysates, arginine is first removed as the flavanate and the filtrate is treated with Reinecke's acid,



The precipitate contains histidine, hydroxyproline, and proline, and is decomposed by suspending in methyl alcohol and treating with copper sulphate which precipitates the Reinecke acid. Excess copper is removed with hydrogen sulphide and sulphuric acid with baryta; addition of picrolonic acid now precipitates histidine which can be recovered as the dihydrochloride (12.2 g. from 250 g. hæmoglobin) by decomposing the precipitate with concentrated hydrochloric acid, filtering and evaporating. The hydroxyproline and proline can be separated with cadmium chloride which precipitates the latter. For the separation of histidine from hydrolysed blood corpuscle paste by Foster and Schmidt's method of electrical transport (*J. Amer. Chem. Soc.* 1926, **48**, 1709), see Cox, King and Berg, *J. Biol. Chem.* 1929, **81**, 755. Since cystine is precipitated by silver oxide at  $p_H$  6 it may occur in the crude histidine fractions from proteins; its copper salt, however, is very insoluble and these fractions may be freed from cystine by boiling with copper hydroxide, cooling and filtering (Vickery and Leavenworth, *ibid.* 1929, **83**, 523). For the separation of histidine from histamine and choline by electrodialysis, and also the recovery of the base from the dipicrate, platinichloride, etc., by this method, see Gebauer-Fülneegg and Kendall, *Ber.* 1931, **64** [B], 1067. Quantitative separation of histidine from arginine may be obtained by adding an excess of a soluble silver salt and adjusting the  $p_H$  value to 7.0 by careful addition of barium hydroxide solution. A second precipitation as the silver compound gives histidine free from arginine. The latter is precipitated as the silver salt at  $p_H$  10–11. The histidine is



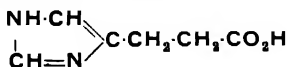
conveniently recovered from the precipitate by decomposition with hydrochloric acid (Vickery and Leavenworth, *J. Biol. Chem.* 1927, **72**, 403; **75**, 115; see also Rosedale, *Biochem. J.* 1929, **23**, 161). According to Bussit (*Bull. Soc. Chim. biol.* 1934, **16**, 727), Hopkin's mercuric sulphate reagent does not give quantitative separation from arginine. Separation of histidine from tyrosine may be effected by means of a reagent containing mercuric chloride, sodium acetate and sodium chloride, tyrosine remaining in solution (Lang, *Z. physiol. Chem.* 1933, **222**, 3).

The constitution of histidine as  $\alpha$ -amino- $\beta$ -glyoxaline-5-propionic acid, has been established by the work of Fränkel, Pauly, Knoop and Windaus, and of Pyman. Fränkel (*Monatsh.* 1903, **24**, 229) showed that histidine contains a carbonyl-group, since it displaces carbon dioxide from silver and copper carbonates, and an amino-group because on treatment with hypobromite or nitrous acid one nitrogen atom is removed and a hydroxyl group introduced. Fränkel therefore represented histidine by the partly expanded formula



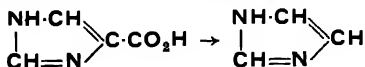
and gave the name *histine* to the complex  $\text{—C}_5\text{H}_6\text{N}_2\text{—}$ , and *hydroxydeaminohistidine* or *hydroxyhistinecarboxylic acid* to the compound,  $\text{HO-C}_5\text{H}_6\text{N}_2\text{-CO}_2\text{H}$ , obtained from histidine by the action of nitrous acid. Pauly (*Z. physiol. Chem.* 1904, **42**, 513) confirmed the presence of the carboxyl group in histidine by preparing the methyl ester, and proved that the histine complex  $\text{—C}_5\text{H}_6\text{N}_2\text{—}$  contains an imino group, because histidine yields a dinaphthalene-sulphonyl derivative, and forms a red dye with diazobenzenesulphonic chloride. These considerations, and the stability of the compound, led Pauly to conclude that the complex *histine* contains an iminazole (glyoxaline) ring, and that histidine has the constitution I.

This conclusion has been confirmed by Knoop and Windaus (*Beitr. chem. Physiol. Path.* 1905, **7**, 144), who obtained *glyoxaline-5-propionic acid* (iminazoly-5-propionic acid),



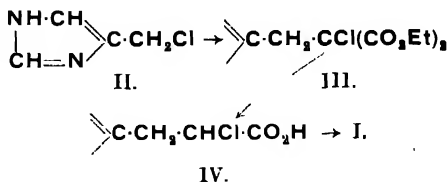
by reducing Fränkel's hydroxyhistinecarboxylic acid, and showed that it was identical with the synthetic product prepared by the action of formaldehyde and ammonia on Wolff's glyoxyl-propionic acid (*Annalen*, 1890, **260**, 79). (*Cf.* Fränkel (*Beitr. chem. Physiol. Path.* 1907, **19**, 116).

Knoop (*ibid.* 1907, **10**, 111) also showed that by the successive oxidation of hydroxyhistinecarboxylic acid, glyoxaline-5-carboxylic acid is obtained which, when heated at  $286^\circ$ , loses carbon dioxide and yields glyoxaline,



The complete synthesis of histidine is described by Pyman (*J.C.S.* 1911, **99**, 1386). 5-Chloro-

methylglyoxaline (II), obtained from diaminoacetone (*ibid.* 668), condenses with ethyl sodiochloromalonate to form the compound III. This ester on hydrolysis is converted into *dl*- $\alpha$ -chloro- $\beta$ -glyoxaline-5-propionic acid (IV), which reacts with ammonia to form *dl*-histidine (I),



Pyman (*ibid.* 1916, **109**, 186) also synthesised *dl*-histidine from benzoyl-*dl*-histidine (see below) by boiling this for 4 hours with 20% aqueous hydrochloric acid.

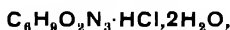
Histidine gives the biuret reaction (Herzog, *Z. physiol. Chem.* 1903, **37**, 248). It also gives the Weidel pyrimidine reaction (Fränkel, *l.c.*). With diazobenzenesulphonic chloride in the presence of sodium carbonate, histidine gives a dark cherry-red coloration, becoming orange on the addition of an acid (Pauly, *Z. physiol. Chem.* 1904, **42**, 508; 1915, **94**, 427). This is a very sensitive test for iminazole derivatives, and amongst the products of protein hydrolysis only histidine and tyrosine give this reaction. It may be used to detect histidine in the presence of tyrosine after addition of benzoyl chloride (Inouye, *ibid.* 1913, **83**, 79) or after a preliminary separation with mercuric chloride (Lang, *l.c.*). If the coloured solution obtained by Pauly's reaction is reduced, e.g. with zinc dust and hydrochloric acid, and then made strongly alkaline with ammonia, the presence of histidine is indicated by the formation of a bright golden-yellow colour (Totani, *Biochem. J.* 1915, **9**, 385). Histidine develops a yellow colour with bromine water; this disappears on warming but after a time a pale red colour appears, which afterwards deepens to a wine-red. The reaction is sensitive to concentrations of 1:1,000 but is vitiated by too large excess of bromine water (Knoop, *Beitr. chem. Physiol. Path.* 1908, **11**, 356). For testing urine, the reaction is best conducted in faintly acid solution (Armstrong and Walker, *Biochem. J.* 1932, **26**, 143); for further improvements, see Hunter, *Amer. Chem. Abstr.* 1923, **17**, 574; *cf. ibid.* 1936, **30**, 7604. Bromination of histidine in 33% acetic acid gives a black substance which dissolves in concentrated ammonia with a purple-red, and in ammonium carbonate with a strong blue-violet coloration, the intensity of which is proportional to the concentration of histidine. This reaction is sensitive to 1:50,000 and is specific, but histamine gives a weak golden-yellow and methylhistidine a very pale reddish-violet colour (Kapeller-Adler, *Biochem. Z.* 1933, **264**, 131).

Colorimetric methods of estimating histidine based on Pauly's and Kapeller-Adler's reactions have been devised. Thus diazotised sulphanilic acid is used by Weiss and Sobolev (*Biochem. Z.* 1913, **58**, 119) in the presence of sodium carbonate and comparison is made with an identi-

cally treated standard histidine solution. See also Loeper, Leasure and Thomas, *Bull. Soc. Chim. Biol.* 1934, **16**, 1385. Suzuki and Kaishio (*Bull. Agric. Chem. Soc. Japan*, 1927, **3**, 33) use sodium hydroxide as the alkali and compare the golden-yellow colour with  $N/100$  potassium dichromate. The microdetermination by Pauly's reaction using a photometer with a filter (S53) is described by Lang (*Z. physiol. Chem.* 1933, **222**, 3). The reaction is inhibited by glycine, aspartic acid and uric acid, but this may be overcome by adding larger quantities of the reagent. Urea does not interfere (Meshkova, *ibid.* 1936, **240**, 199). Diazotised *p*-nitraniline has been suggested as a reagent for the determination of histidine in blood (Barac, *Compt. rend. Soc. Biol.* 1935, **118**, 198; 1935, **119**, 545). Kapeller-Adler's method cannot be applied to the direct determination of histidine in urine owing to the inhibition by phosphates, etc., and so a preliminary separation, e.g. with Hopkin's reagent (*Biochem. Z.* 1933, **264**, 131) or with magnesium chloride in alkaline solution (lojo, *Diagnostica tec. lab. (Napoli) Riv. mensile*, 1936, **7**, 8) is necessary. For the use of the step-photometer in this method, see Kapeller-Adler, *Biochem. Z.* 1934, **271**, 206. Fohn's method for the determination of amino-acids in blood gives low values owing to incomplete precipitation of the proteins by tungstic-sulphuric acids. Phosphotungstic acid or, better, trichloroacetic acid gives much smaller errors (Re and Potick, *Rev. soc. argentina Biol.* 1929, **5**, 725; *Compt. rend. Soc. Biol.* 1930, **103**, 1283; see also Wechsler, *Z. physiol. Chem.* 1911, **73**, 141). A modification of the Van Slyke method in which the histidine is estimated colorimetrically is described by Cavett (*J. Biol. Chem.* 1932, **45**, 335); other modifications are due to Russo (*Boll. Soc. Ital. Biol. sperim.* 1927, **2**, 174) and Davies (*Biochem. J.* 1927, **21**, 815, 1920). For a modification of Hanke and Kocessler's method (*Amer. Chem. Abstr.* 1920, **14**, 3687) of determining histidine, see Jorpes (*Biochem. J.* 1932, **26**, 1507); and for its estimation in small quantities of protein by precipitation with mercuric sulphate after alkaline hydrolysis, see Rosedale and Da Silva (*ibid.* 1932, **26**, 369); and by bromination after hydrolysis, see Thrun and Trowbridge (*J. Biol. Chem.* 1918, **34**, 343). For a microchemical method, see Kober and Sugiura, *J. Amer. Chem. Soc.* 1913, **35**, 1546; and Van Slyke, *J. Biol. Chem.* 1915, **23**, 411, *cf. ibid.* 1911, **9**, 185; **10**, 29; 1912, **12**, 279. Histidine can also be determined volumetrically by titration with titanium trichloride of the dye formed in the Pauly reaction (Lautenschlager, *Z. physiol. Chem.* 1918, **102**, 226).

*dl*-Histidine is obtained by racemisation of the naturally occurring *l*-form, for example by heating under pressure (Abderhalden and Weil, *ibid.* 1912, **77**, 435), or with 20% hydrochloric acid at 160° (Fränkel, *Beitr. chem. Physiol. Path.* 1906, **8**, 160); it crystallises in quadrilateral plates and decomposes at 283° (corr.) (Pyman, *J.C.S.* 1911, **99**, 1397). *dl*-Histidine can be resolved by the fractional crystallisation of its salts with *d*-tartaric acid into the *d*- and *l*-isomers, and the *l*-histidine so obtained is identical with the naturally occurring com-

pound. Partial resolution can be obtained by means of yeast, the *d*-isomer remaining unattacked (Abderhalden and Weil, *Z. physiol. Chem.* 1912, **77**, 435; Ehrlich, *Biochem. Z.* 1914, **63**, 379). The spontaneous resolution of histidine hydrochloride has been described by Duschinsky (*Chem. and Ind.* 1934, **53**, 10). Thus, a hot mixture of pure *l*- and *dl*-histidine hydrochlorides with 1.5 parts of water, when cooled rapidly to 20° and quickly filtered, gives the *l*-salt; addition of alcohol and ether to the mother liquor and further cooling to 0° yields almost pure *dl*-salt, while concentration of the filtrate and rapid cooling to 20° gives almost pure *d*-salt. *dl*-Histidine monohydrochloride,



has m.p. 117–119° (corr.); the *sesquihydrochloride*,  $(\text{C}_6\text{H}_9\text{O}_2\text{N}_3)_2 \cdot 3\text{HCl} \cdot \text{H}_2\text{O}$ , has m.p. 168–170° (corr.); the *dihydrochloride*, m.p. 235–236° (corr.); the *picrate*,  $\text{C}_{12}\text{H}_{12}\text{O}_9\text{N}_6 \cdot \text{H}_2\text{O}$ , decomposes at 180–181° (corr.); the *dipicrate*,  $\text{C}_{18}\text{H}_{15}\text{O}_{18}\text{N}_9 \cdot 2\text{H}_2\text{O}$ , decomposes at 190° (corr.) (Pyman, *J.C.S.* 1911, **99**, 339; *cf.* 1916, **109**, 196).

*d*-Histidine crystallises in monoclinic plates forming elongated hexagons; it decomposes at 287–288° (corr.), and has  $[\alpha]_D +39.3^\circ$ . *d*-Histidine-*d*-hydrogen tartrate is sparingly soluble, decomposes at 234° (corr.) and has  $[\alpha]_D +13.3^\circ$  (Pyman, *ibid.* 1911, **99**, 1937; 1916, **109**, 197); *d*-histidine hydrochloride crystallises with  $1\text{H}_2\text{O}$  (Duschinsky, *l.c.*).

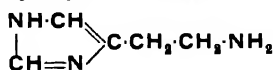
*l*-Histidine is soluble in water, sparingly soluble in alcohol and insoluble in ether (Kossel, *Z. physiol. Chem.* 1896, **22**, 184); it crystallises from water in anhydrous needles or plates, m.p. 287° (corr.),  $n_D^{20}$  1.520,  $n_D$  indeterminate,  $n_D^{25}$  1.610 (Fränkel, *Monatsh.* 1903, **24**, 229; Keenan, *J. Biol. Chem.* 1929, **83**, 137); for photomicrographs of the crystals from water and 50% alcohol, see Vickery and Leavenworth, *ibid.* 1928, **76**, 701. In aqueous solution it has a sweet taste (Pyman, *J.C.S.* 1911, **99**, 1397), is feebly alkaline (Hedin, *Z. physiol. Chem.* 1896, **22**, 191) and is optically active,  $[\alpha]_D^{20} -39.74^\circ$  (Kossel and Kutscher, *ibid.* 1899, **28**, 382; Duschinsky, *l.c.*; *cf.* Pyman, *l.c.*). The isoelectric point occurs at  $p_H$  7.64; the dissociation constants at 25° (expressed as logarithms,  $p_K$ ) are 1.77 ( $\text{CO}_2\text{H}$ ), 6.0 (iminazole), 9.0 ( $\text{NH}_2$ ) (Schmidt, Appleman and Kirk, *J. Biol. Chem.* 1929, **85**, 177; Levy, *ibid.* 1935, **109**, 361; Birch and Harris, *Biochem. J.* 1930, **24**, 564; and *Amer. Chem. Abstr.* 1932, **26**, 485). For the ultra-violet absorption spectrum of *l*-histidine and comparison with that of histamine, see Ellinger, *Biochem. Z.* 1929, **215**, 279; Becker, *Arch. ges. Physiol. (Pflüger's)*, 1931, **228**, 751; Hicks and Holden, *Austral. J. Exp. Biol.* 1932, **10**, 49, and in the long-range ultra-violet, Ellinger, *Biochem. Z.* 1932, **248**, 437; for the infra-red absorption between  $\lambda=0.8\mu$  and  $\lambda=8\mu$ , see Heintz, *Compt. rend.* 1935, **201**, 1478. Irradiation of histidine with ultra-violet light causes decomposition in a number of ways. Thus, under conditions favouring oxidation,

elimination of ammonia appears to be the main reaction and may account for 90% of the histidine decomposed (Lieben and Urban, *Biochem. Z.* 1931, **239**, 250); the residue of the molecule becomes iminazoylactaldehyde (Szendri, *Arch. ges. Physiol. (Pflüger's)*, 1931, **228**, 743). In the absence of oxygen, decarboxylation to histamine takes place and has been demonstrated by isolation and characterisation of the base (7 mg. from 1 g.) (Holtz, *Klin. Woch.* 1933, **12**, 1613; *Arch. exp. Path. Pharm.* 1934, **175**, 97) and by pharmacological tests (Bourdillon, Gaddum and Jenkins, *Proc. Roy. Soc.* 1930, B, **106**, 388). For this reaction light of wave-length shorter than 2,650Å. is much more active than the longer wave-lengths, also the effect is slight in acid solution but very intense in alkaline (Lieben, *Biochem. Z.* 1927, **184**, 453; Bourdillon *et al.*, *l.c.*). Histidine (and other amino-acids) is adsorbed from aqueous solution on activated carbon, a very marked maximum being shown at the isoelectric point (Phelps and Peters, *Proc. Roy. Soc.* 1929, A, **124**, 554; Ito, *J. Agric. Chem. Soc. Japan*, 1936, **12**, 204).

When histidine is administered as a food, or by intravenous injection, very little (0.4 g. out of 10 g.) is recoverable as such from the urine; the creatinine (Abderhalden and Buaclze, Z. physiol. Chem. 1931, 200, 87), urea and ammonia in the urine are largely increased but the increase of allantoin is very slight (Abderhalden, Einbeck and Schmid, *ibid.* 1909, 62, 322; 1910, 68, 395; Abderhalden, *ibid.* 1919, 74, 481; Abderhalden and Weil, *ibid.* 1912, 77, 435; Kowalewsky, Biochem. Z. 1909, 23, 1). Both *d*- and *l*-forms are utilised in the animal organism, but the *d*-form is rather less efficient in promoting the growth of rats on a histidine-deficient diet (Cox and Berg, J. Biol. Chem. 1934, 107, 497). The *d*-form can be obtained from the urine of rabbits fed on *dl*-histidine. Histidine markedly increases the glycogen mobilisation effect of adrenaline (Taniuchi, Folia pharmacol. japon. 1930, 10, No. 164), and also reduces the coagulation time of blood (Burger, Klin. Woch. 1936, 15, 550). It appears to be the precursor of the erythema-causing irritant which is formed in the human skin during exposure to ultra-violet light (Frankenburger and Zimmermann, Naturwiss. 1933, 21, 116). It has been found of use in the treatment of gastric and duodenal ulcers (Weiss and Aron, Compt. rend. Soc. Biol. 1933, 112. 1530; Eads, Amer. J. Digest. Dis. Nutr 1935, 2, 426); and in conjunction with tryptophan, in the treatment of hay-fever (Lenormand, Presse méd. 1933, 41, 1141). For the catabolism of histidine in the animal organism, see Dakin and Wakeman, J. Biol. Chem. 1912, 10, 499, and as the forerunner of purine bodies in animal metabolism, see Ackroyd and Hopkins (Biochem. J. 1916, 10, 551).

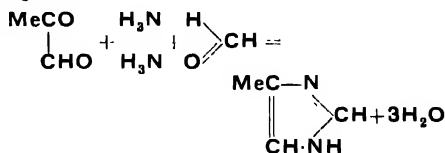
l-Histidine administered subcutaneously to rabbits is excreted as urocanic acid (iminazoyl acrylic acid). The fungus, *Oidium lactis*, converts it into the saturated iminazoylpropionic acid (Kiyokawa, Z. physiol. Chem. 1933, 214, 38). When histidine undergoes anaerobic bacterial cleavage by the action of putrefying pancreas, it is converted almost quantitatively by the loss

of carbon dioxide into 5- $\beta$ -aminoethylglyoxaline ( $\beta$ -iminazolyethylamine, *histamine*),

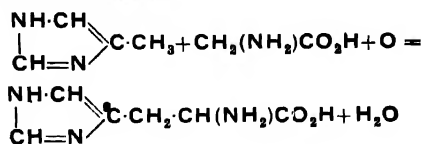


*iminazoly-5-propionic acid* (v. p. 233b), being the other product (see Ackermann, Z. physiol. Chem. 1910, **65**, 504). The 5- $\beta$ -aminoethylglyoxaline thus obtained is identical with the base prepared synthetically by Windaus and Vogt (Ber. 1907, **40**, 3691) from ethyl iminazolypropionate or by Pyman (J.C.S. 1911, **99**, 608) from diaminoacetone, and is also identical with the ergot base *histamine* isolated by Barger and Dale (Phil. Trans. 1910, 2592) which is also present in Popielski's *vasodilatin* (Barger and Dale, J. Physiol. 1911, **41**, 499); see Mellanby and Twort (J. Physiol. 1912, **45**, 53) who isolated a bacillus of the colon group which splits off carbon dioxide from histidine and converts it to histamine. *Bacillus coli communis* transforms histidine into histamine to the extent of 50% in the presence of glycerol or dextrose and potassium nitrate or ammonium chloride (Koessler and Hanke, J. Biol. Chem. 1919, **39**, 539; 1920, **43**, 529, 543). Raistrick (Biochem. J. 1917, **11**, 71; 1919, **13**, 446), found that bacteria of the *Coli*-typhus group convert histidine into urocanic acid in certain media. *L*-Histidine is converted to the extent of 11% into *d*- $\beta$ -iminazolyllactic acid by the prolonged action of *Proteus vulgaris* in a protein-free nutrient medium (Hirni, Acta Schol. Med. Kioto, 1919, **3**, 49).

A possible explanation of the formation of histidine in the plant economy is afforded by the work of Knoop and Windaus (Beitr. chem. Physiol. Path. 1905, **6**, 292; Ber. 1906, **39**, 3886; 1907, **40**, 799) on the synthetic formation of iminazole derivatives from sugars and ammonia. These authors find that when a solution of glucose containing zinc hydroxide dissolved in ammonia is exposed to sunlight at the ordinary temperature for some weeks, it is converted to the extent of 10% into 5-methyliminazole. It is probable that methylglyoxal and formaldehyde are produced as intermediate products and then react with the ammonia according to the equation



*d*-Mannose, *d*-fructose, *d*-sorbose, *l*-arabinose or *l*-xylose also yield methyliminazole when similarly treated. The authors suggest that histidine may be formed naturally by the condensation of methyliminazole with glycine, and simultaneous oxidation:



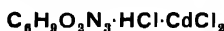
Enzymes from the liver of various animals cause decomposition of histidine with elimination of ammonia (Kauffmann and Mislowitz, *Biochem. Z.* 1930, **226**, 325; 1931, **234**, 101); the same type of decomposition is induced by boiling with bone black (Lieben and Benek, *ibid.* 1935, **280**, 88). Electrolytic oxidation of histidine leads to the formation of carbon dioxide, ammonia and malonic acid, probably through the intermediate formation of aspartic acid (Takayama and Oeda, *J. Chem. Soc. Japan*, 1934, **55**, 649; *Bull. Chem. Soc. Japan*, 1934, **9**, 535). Oxidation with sodium hypochlorite or hydrogen peroxide or permanganates causes liberation of carbon dioxide and ammonia (Herzog, *Z. physiol. Chem.* 1903, **37**, 248; Karyagina, *Arch. Sci. biol. U.S.S.R.* 1935, **37**, 372 (in German, 376); Lieben and Bauninger, *Biochem. Z.* 1933, **261**, 387). Oxidation with dichromate and sulphuric acid yields acetic and hydrocyanic acids (Frankel, *Beitr. chem. Physiol. Path.* 1906, **8**, 159). Sodium hypochlorite (1 mol.) converts histidine monohydrochloride into iminazoly-5-acetaldehyde (Langheld, *Ber.* 1909, **42**, 2373; *Chem. Zentr.* 1910, **11**, 1104). For the rate of reaction with formaldehyde in 0.1*N*-sodium hydroxide at 37°, see Holden and Freeman, *Austral. J. Exp. Biol.* 1931, **8**, 189. When warmed with acetic anhydride in pyridine, carbon dioxide (1 mol.) is liberated and the product, when evaporated with 10% hydrochloric acid, gives colourless prisms, m.p. 205–206°, of 4-iminazoly-3-amino-butan-2-one dihydrochloride,



(Dakin and West, *J. Biol. Chem.* 1928, **78**, 745). *L*-Histidine forms stable salts with acids and their solutions are dextrorotatory.

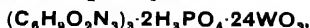
**Monohydrochloride**,  $\text{C}_6\text{H}_9\text{O}_2\text{N}_3\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , forms large colourless rhombic crystals, *a:b:c* = 0.7965:1:1.7110, has  $[\alpha]_D^{20} +1.74^\circ$ , m.p. 80°, and loses water at 140° (Kossel, *Z. physiol. Chem.* 1896, **22**, 176; Hedin, *ibid.* p. 191; Bauer, *ibid.* pp. 182, 285; Kossel and Kutscher, *ibid.* 1899, **28**, 382; Fränkel, *Monatsh.* 1903, **24**, 229). It is fairly soluble in water, insoluble in alcohol and ether (Herzog, *Z. physiol. Chem.* 1896, **22**, 193). The **dihydrochloride**,  $\text{C}_6\text{H}_9\text{O}_2\text{N}_3\cdot 2\text{HCl}$ , forms rhombic tables, *a:b:c* = 0.76537:1:1.77516, isomorphous with the monohydrochloride (Kossel and Kutscher, *l.c.*; Schwantke, *ibid.* 1899, **28**, 386; 1890, **29**, 492); it has m.p. 196° (245°, Kossel and Kutscher, *l.c.*) and  $[\alpha]_D^{20} +7.6^\circ$  (Abderhalden and Einbeck, *ibid.* 1909, **62**, 330).

#### *Histidine Cadmium Chloride*,

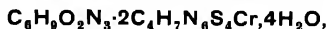


melts and decomposes at 270–275°, is very soluble in water but almost insoluble in hot or cold methyl or ethyl alcohol (Sehenck, *ibid.* 1904, **43**, 73; cf. Kutscher, *Chem. Zentr.* 1908, **1**, 404). Histidine gives a complex copper salt,  $\text{Cu}(\text{C}_6\text{H}_9\text{O}_2\text{N}_3)_2$  (Kober and Sugjura, *J. Biol. Chem.* 1913, **13**, 5), and a compound with iron,  $\text{Fe}(\text{C}_6\text{H}_9\text{O}_2\text{N}_3)_2$  (G.P. 266522).

#### *Histidine Phosphotungstate*,

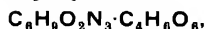


crystallises without water of crystallisation (Wechsler, *Z. physiol. Chem.* 1911, **73**, 140). The **nitrate**,  $\text{C}_6\text{H}_9\text{O}_2\text{N}_3\cdot 2\text{HNO}_3$ , crystallises in prisms from water, m.p. 149–152° (Fränkel, *Monatsh.* 1903, **24**, 243). The **reineckate**,



is precipitated from a solution made acid to Congo Red. Its solubility, 0.2948–0.3044 g. in 100 c.c. is greater than that of the carnosine compound and it can be used for their separation (Smorodincev, *Biochem. Z.* 1930, **222**, 425). The **monopicrotonate**,  $\text{C}_6\text{H}_9\text{O}_2\text{N}_3\cdot\text{C}_{10}\text{H}_8\text{O}_5\text{N}_4$ , crystallises in yellow needles (Kossel and Pringle, *Z. physiol. Chem.* 1905, **49**, 319; Weiss, *ibid.* **52**, 113; Brigl, *ibid.* 1910, **64**, 337, 339; Steudel, *ibid.* 1905, **44**, 157); 1 part is soluble in 150 parts of water; the **dipicrotonate** is orange. The **di-m-bromopicrotonate** decomposes at 216–218° (Zimmermann and Cuthbertson, *ibid.* 1932, **205**, 38). The **dipicrate**,  $\text{C}_{18}\text{H}_{15}\text{O}_{16}\text{N}_9\cdot 2\text{H}_2\text{O}$ , has m.p. 86° (corr.) (Pyman, *J.C.S.* 1911, **99**, 343); the pentahydrate,  $\text{C}_{18}\text{H}_{15}\text{O}_{16}\text{N}_9\cdot 5\text{H}_2\text{O}$ , has m.p. 80° (Hugounenq and Florence, *Bull. Soc. Chim. biol.* 1919, **1**, 102). The **di-2,4-dinitro-1-naphthol-7-sulphonate** separates in yellow needles containing  $\frac{1}{2}\text{H}_2\text{O}$  and decomposing at 251–254°, depending on the rate of heating. The free base or its salts can be recovered by decomposing the compound with dilute acid and extracting the reagent with butyl alcohol (Vickery, *J. Biol. Chem.* 1927, **71**, 303). The **2:6-diiodo-1-phenol-4-sulphonate** (sozoiiodolate) decomposes at 207–208° and 1.938 g. dissolve in 100 g. of water at 16° (Ackermann, *Z. physiol. Chem.* 1934, **225**, 46). The **rufanate** (quinizarin-2-sulphonate) is sparingly soluble in water but the base can easily be liberated with baryta (Zimmermann, *ibid.* 1930, **188**, 180).

#### *L-Histidine-d-hydrogen Tartrate*,



is easily soluble in water, crystallises in large well-defined prisms, and decomposes at 172–173° (corr.) and has  $[\alpha]_D^{20} +16.3^\circ$ . **L-Histidine-l-hydrogen tartrate** is sparingly soluble in cold water, crystallises in clusters of prisms and decomposes at 234° (corr.), and has  $[\alpha]_D^{20} -12.1^\circ$  (Pyman, *J.C.S.* 1911, **99**, 1397, 1400).

The histidine silver compound is formed as an amorphous precipitate which, at 100°, has the composition  $\text{Ag}_2\text{C}_6\text{H}_9\text{O}_2\text{N}_3\cdot\text{H}_2\text{O}$ ; it is soluble in ammonia (Hedin, *Z. physiol. Chem.* 1896, **22**, 194).

#### DERIVATIVES.

##### *Histidine Methyl Ester Hydrochloride*,



forms flat rhombic prisms, m.p. 196° (decomp.); the free ester is an oil (Pauly, *ibid.* 1904, **42**, 508; Fischer and Cone, *Annalen*, 1908, **363**, 108). **Histidine anhydride**,  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_6$ , forms glittering prisms, m.p. 340° (Fischer and Suzuki, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, **1333**; cf. Abderhalden and Geidel, *Fermentforsch.* 1931, **12**, 518); the *L*-anhydride has m.p.

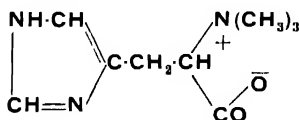
328° in a closed evacuated tube, crystallises with  $2\frac{1}{2}\text{H}_2\text{O}$ , and has  $[\alpha]_D^{20} -66.24^\circ$  in normal hydrochloric acid solution; the *dl*-anhydride also has m.p. 328°, and is obtained by heating the ethyl ester of histidine at 160° (Pauly, Z. physiol. Chem. 1910, **64**, 75); the *picrate* decomposes at 255° (corr.); the *hydrochloride* at 320°. *Chlorohistidinecarboxylic acid* ( $\alpha$ -chloro- $\beta$ -iminazolypropionic acid) forms thick prisms, m.p. 191° (decomp.), the corresponding racemic compound decomposes at 201° (corr.) (Pyman, J.C.S. 1911, **99**, 1394), the *oxalate* of the *ethyl ester* has m.p. 161° (Windaus and Vogt, Beitr. chem. Physiol. Path. 1908, **11**, 406). *N*-Carbobenzyl-*oxy*-1-histidine,

$\text{C}_3\text{H}_3\text{N}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\text{NH}\cdot\text{COOCH}_2\cdot\text{C}_6\text{H}_5$  has m.p. 209° (Bergmann and Zervas, Ber. 1932, **65** [B], 1192). *N*:*N'*-histidine-disulphonic acid is obtained in the form of potassium salts by the action of *N*-pyridiniumsulphonic acid and potassium carbonate on histidine at +10° (Baumgarten, Marggraff and Dammann, Z. physiol. Chem. 1932, **209**, 145).

*dl*-3-Methylhistidine is formed during the hydrolysis of anserine (*q.v.*) with baryta; it decomposes at 248–252° with foaming and the nitrate decomposes at 144–146° (Linneweh, Keil and Hoppe-Seyler, *ibid.* 1929, **183**, 11). *L*-3-Methylhistidine is obtained if the hydrolysis of anserine is carried out with 20% sulphuric acid; it crystallises with  $1\text{H}_2\text{O}$ , m.p. 248–249°,  $[\alpha]_D^{18} -25.98^\circ$ ; nitrate, m.p. 216°; picrolonate, m.p. 246°, sintering at 240° (Linneweh and Linneweh, *ibid.* 1930, **189**, 80).

Direct methylation of histidine affects the glyoxaline ring. Under certain conditions there may be obtained *pentamethylhistidine* which forms a stable chloride and a sparingly soluble aurichloride,  $\text{C}_{11}\text{H}_{21}\text{O}_2\text{N}_5\text{Au}_2\text{Cl}_6$ , m.p. 220°, but which does not respond to the diazo-reaction (Engeland and Kutscher, Chem. Zentr. 1913, **I**, 28).

*Trimethylhistidine* (*herzynine*), the *betaine* corresponding to histidine,



occurs in fungi, *e.g.* in *Boletus edulis* (Wintersteiner and Reuter, Z. physiol. Chem. 1913, **86**, 234), it is not known in the free state, but has been isolated as the aurichloride,



m.p. 183° (decomp.) (Engeland and Kutscher, *l.c.*; Zentr. Physiol. 1912, **26**, 569). Barger and Ewins (Biochem. J. 1913, **7**, 204) proved the identity of specimens obtained from various sources. The *picrate* has m.p. 201–202°, the *dipicrate*, m.p. 213–214° and the *picrolonate*, m.p. 229–230°. See also Barger and Ewins, J.C.S. 1911, **99**, 2340; Küng, Z. physiol. Chem. 1914, **91**, 249.

*Formyl-1-histidine* is formed when histidine is heated with anhydrous formic acid (Fischer

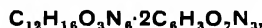
and Cone, Annalen, 1908, **363**, 116); it crystallises in needles from methyl alcohol, m.p. 203° (decomp.), is very easily soluble in water, and gives a deep red colour with diazotised sulphaphanic acid. *Benzoyl-1-histidine*, obtained by the Schotten-Baumann method, forms colourless crystals +  $1\text{H}_2\text{O}$ , m.p. 249° (decomp.) (Pauly, *l.c.*; Fränkel, *l.c.*; Gerngross, Z. physiol. Chem. 1920, **108**, 54); it is insoluble in water and organic solvents but easily soluble in alkalis. In a solution faintly alkaline with sodium hydroxide, it smoothly takes up 2 atoms of iodine on the carbon atoms of the iminazole ring (Strauss and Maschmann, Ber. 1935, **68** [B], 1108; Pauly, Ber. 1910, **43**, 2243). *Benzoyl-dl-histidine* (from  $\alpha$ -benzoylamino- $\beta$ -iminazolyacrylic acid on reduction with sodium amalgam in aqueous suspension), has m.p. 248° (corr. decomp.); it crystallises in hard, glistening prisms with  $1\text{H}_2\text{O}$ , which is lost at 115°. The *hydrochloride* crystallises from water in hard, glistening prisms, m.p. 232° (corr., foaming). The *picrate* crystallises in bunches of yellow feathery needles, m.p. 226° (corr.) (Pyman, J.C.S. 1916, **109**, 195). Benzoylation of histidine methyl ester yields a tribenzoyl derivative,



m.p. 219° (not sharp), which does not give the red colour with diazotised sulphaphanic acid; on heating, the iminazole ring closes again and the product gives the characteristic colour reaction (Kossel and Edlbacher, Z. physiol. Chem. 1915, **93**, 396; cf. Inouye, *l.c.*, who points out that in order to obtain the colour reaction excess of benzoyl chloride must not be present). The *azlactone* of *benzoylhistidine* is obtained from benzoylhistidine and hydrazine hydrate and has m.p. 215° (Küster and Iron, *ibid.* 1929, **184**, 225). *p*-Nitrobenzoylhistidine has m.p. 251–252° (Pauly).  $\alpha$ -Phthalylhistidine is formed by fusing histidine with phthalic anhydride at 180–200°; it has m.p. 188°, *picrate*, m.p. 251°; the methyl ester has m.p. 187° and its *hydrochloride* m.p. 238–240°; the ethyl ester has m.p. 195°. *d*- $\alpha$ -Bromoisohexoyl-1-histidine methyl ester,



*d*- $\alpha$ -bromoisohexoyl-1-histidine,  $\text{C}_{12}\text{H}_{18}\text{O}_3\text{N}_3\text{Br}$ , has m.p. 118° (corr.); *l*-leucyl-1-histidine,  $\text{C}_6\text{H}_9\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{C}_6\text{H}_5\text{N}_2)\text{CO}_2\text{H}$ , crystallises in plates or prisms containing water which is lost at 100°/15–20 mm., and has m.p. 178° (corr. decomp.); the copper salt forms deep violet crystals; *glycyl-1-histidine* melts at 130–155°; *dl*-alanyl-1-histidine crystallises with  $1\text{H}_2\text{O}$  (Abderhalden and Geidel, *l.c.*); *l*-histidyl-1-histidine forms a lemon-yellow *picrate*,



which crystallises from water in prisms; on heating *in vacuo* at 80° it becomes orange-yellow and has m.p. 165–175° (Fischer and Suzuki, *l.c.*).

M. A. W.

HISTOZYME (v. Vol. IV, 315a).

HITTORF TRANSPORT (OR TRANSFERENCE) NUMBER. When an electric current is passed through a solution of an electrolyte, equivalent quantities of each ion are discharged at the electrodes, as required by

Faraday's law. The current, however, is not usually carried equally by the two ions, since the ions move at different speeds. This gives rise to an unequal change in quantity of electrolyte round each electrode. The loss of electrolyte round each electrode is proportional to the speed of the ion moving away from the electrode. The transport (or transference) number of an ion gives the fraction of the total current carried by that ion.

If  $u$  and  $v$  are the mobilities of the cation and anion respectively (i.e. their velocities in cm. per sec. for a potential gradient of 1 volt per cm.) the transport numbers of the cation,  $n_c$ , and of the anion,

$$n_a = \frac{u}{u+v} \quad \text{and}$$

$n_a = \frac{v}{u+v}$  Alternative symbols are  $I_c$  and  $I_a$ .

Since  $n_c + n_a = 1$ , it is necessary to know only one of these in order to calculate the other, and very often the anion transport number is called simply the "transport number," and denoted by  $n$ .

Unlike the mobilities of the separate ions, the transport number varies from salt to salt, e.g. the transport number of the  $\text{Cl}'$  ion is different for  $\text{KCl}$  and  $\text{NaCl}$ . It is clear that by measuring the quantity of electrolyte present round an electrode before and after electrolysis, the transport number,  $n$ , can be calculated.

There are various types of apparatus in use (see H. S. Taylor, "Physical Chemistry," Macmillan, 1930, Vol. 1, p. 680; A. Findlay, "Practical Physical Chemistry," 7th ed., Longmans Green, 1935, p. 186). Fig. 1 is a diagram of the apparatus used by Nernst and Loeb (Z. physikal. Chem. 1888, 2, 948). All types of apparatus utilise the same principles, which are as follows:

A quantity of electricity, measured by a coulometer in series with the apparatus, is passed through a solution of an electrolyte of known concentration. The solutions (anolyte and catholyte) round the electrodes are separated to prevent mixing, convection and heating of the solution being minimised by using a weak current (0.01–0.02 amp.) for two hours or more. At the end of this time, the liquid in the anode or cathode compartment is withdrawn and analysed. The liquid between the anode and cathode is also withdrawn and analysed, and should not have changed in composition. Any change indicates that mixing has occurred.

It is advisable, where possible, to prevent the evolution of gas bubbles. A soluble anode, e.g.  $\text{Cu}$  in  $\text{CuSO}_4$ ,  $\text{Ag}$  in  $\text{AgNO}_3$ , is thus often used, but in the calculation of transport numbers account must be taken of the metal dissolved from the anode.

In the case of the alkali halogenides, gases are evolved at both electrodes. The evolution of hydrogen can be avoided by using a mercury cathode covered with a solution of zinc chloride or copper nitrate. If a cadmium anode is used for the electrolysis of sodium chloride solution, cadmium chloride is formed at the anode, and the  $\text{Cd}^{++}$  ions migrate to the cathode. However, they move much more slowly than the  $\text{Na}^{+}$

ions, and do not catch up with the latter. At the cathode, all the  $\text{Cl}'$  ions have migrated away, and are replaced by  $\text{OH}'$  ions from the water, and as these are fast ions, there is mixing. Hydrogen is evolved, but as it rises from the cathode in the upper part of the apparatus, mixing does not occur in the bulk of the solution.

In his original work Hittorf (Ann. Physik, 1858, 103, 1) employed membranes to separate the anolyte and catholyte. It was found by Bein that such membranes may influence the speed of the ions, and they are no longer used.

Hittorf (l.c.), Lenz (Ann. Physik Beibl. 1883, 7, 399) and Jahn (Z. physikal. Chem. 1901, 37, 673) used a ground glass stopper to separate the anolyte and catholyte after the experiment. Weiske (Ann. Physik, 1858, 103, 466) and Rieger

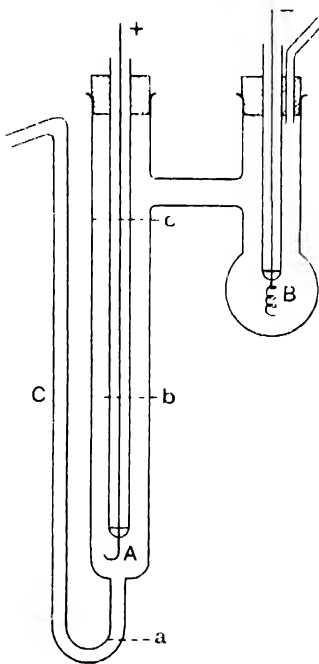


FIG. 1.

used a wide-bore stopcock for this purpose. Noyes (Z. physikal. Chem. 1901, 36, 63) devised an apparatus so that the liquids round the electrodes could be kept neutral during electrolysis by constantly adding acid or alkali. In Findlay's apparatus (A. Findlay, *op. cit.*, Fig. 81) the electrodes are in two bulbs joined by a U-tube, thus decreasing the resistance and minimising heating and convection currents. The calculation for an experiment using the Nernst and Loeb apparatus shown in Fig. 1, which is typical of all types of measurements, is as follows:

The anode A is a thick silver wire sealed into a glass tube which is placed in the longer arm of the vessel. During the experiment the amount of solute around the anode increases, and the heavier layer of solution forms there. B is a cathode of silver foil or wire. The apparatus is placed in a thermostat and the experiments carried out as described above (Nernst and

Loeb, *l.c.*). At the end of the experiment the liquid between *a-b* is forced out of the side arm *C* and analysed. The liquid in the middle compartment *b-c* is also withdrawn and analysed. The total decomposition is obtained from the weight of silver deposited in the silver coulometer in series with the apparatus.

In an experiment 1 g. of the silver nitrate solution contained 0.001136 g.  $\text{Ag}$  and 0.9982 g.  $\text{H}_2\text{O}$ . In electrolysis with a silver coulometer in series, 0.0322 g.  $\text{Ag}$  was deposited in the coulometer and an equal weight therefore dissolved from the anode in the transport apparatus. After the experiment the anode liquid contained 0.03955 g.  $\text{Ag}$  associated with 20.03 g.  $\text{H}_2\text{O}$ . In the original solution this weight of water was associated with 0.02280 g.  $\text{Ag}$ ; hence 0.03955 - 0.02280 = 0.01675 g.  $\text{Ag}$  have been added to the anode liquid. The loss by migration is thus 0.0322 - 0.01675 = 0.01545 g.  $\text{Ag}$ , and the transport number of  $\text{Ag}$  is  $\frac{0.01545}{0.0322} = 0.479$ . That of  $\text{NO}_3$  is 1 - 0.479 = 0.521.

The Hittorf method is satisfactory if the experiment is carefully carried out, but in the case of very dilute solutions a solvent correction is necessary for conducting impurities in the

solvent, which carry part of the total current. If  $\kappa_0$  and  $\kappa$  are the conductivities of the solvent and solution, respectively,

$$n_{\text{corrected}} = n_{\text{observed}} \left(1 + \frac{\kappa_0}{\kappa}\right).$$

When determining transport numbers, the possibility of complex ion formation must be borne in mind. Cadmium iodide shows a transport number greater than unity in concentrated solutions, because the complex ion  $\text{CdI}_4^{2-}$  is formed, and cadmium is carried to, instead of from, the anode.

The modern theory of electrolytes indicates that the transport number is not a true constant, but depends on concentration. The values given below are thus extrapolated to infinite dilution (*cf.* Dole, *J. Physical Chem.* 1931, 35, 3647; Glasstone, "Electrochemistry of Solutions," Methuen, 1937, p. 166).

#### CATION TRANSPORT NUMBERS AT 18° C.

Electrolyte.	Concentration in gram-equivalents per litre.						
	0.005	0.01	0.02	0.05	0.1	0.2	0.5
Lithium chloride .	—	0.332	0.328	0.320	0.313	0.304	—
Sodium chloride .	0.397	0.397	0.396	0.393	0.390	0.385	0.374
Potassium chloride .	0.496	0.496	0.496	0.496	0.495	0.494	0.492
Cadmium iodide .	0.445	0.444	0.442	0.396	0.296	0.127	0.003
Hydrochloric acid .	0.832	0.833	0.833	0.834	0.835	0.837	0.838
Copper sulphate .	—	—	0.375	0.375	0.373	0.361	0.327
Potassium hydroxide .	—	—	—	—	0.265	0.264	0.262
Barium chloride .	—	—	—	0.425	0.421	0.409	0.392

J. R. P.

H. M. T. D. (*v.* Vol. IV, 543*b*).

HOCFEN CEMENT (*v.* Vol. II, 145*b*).

HOCHMANN DEGRADATION (*v.* Vol. II, 375*a*).

HOFMEISTER or LYOTROPIC SERIES (*v.* Vol. III, 286*d*).

HOFSSÄSS BURNER (*v.* Vol. V, 247*a*).

HOLARRHENINE, HOLARRHIMINE, HOLARRHINE (*v.* Vol. III, 322*c*, 323*a*, *d*).

**HOLLANDITE.** A manganese ore of essentially the same composition as psilomelane, but occurring in a crystallised condition, usually as fibrous masses and sometimes as tetragonal crystals. It is a manganate with the general formula  $m\text{R}_2'''\text{MnO}_5 + n\text{R}_4'''(\text{MnO})_3$ , where  $\text{R}''$  is Mn, Ba, K, H, (Fe, Ca, Mg, Na, Co, Ni, Cu), and  $\text{R}'''$  is Mn, Fe, (Al). The extreme values shown in four analyses are:  $\text{MnO}_2$  65.63–75.05,  $\text{MnO}$  5.12–14.20,  $\text{Fe}_2\text{O}_3$  4.43–10.56,  $\text{BaO}$  2.96–17.59,  $\text{K}_2\text{O}$  0.3–3.1,  $\text{H}_2\text{O}$  0–1.10%. The colour is greyish-black, and the lustre submetallic; sp.gr. 4.70–4.95; hardness 4–6. The mineral occurs abundantly in the manganese ore deposits at several places in Central India, and is largely exported from the mines at Sitapár and Balághát. Closely allied minerals, perhaps identical with hollandite, are the crystalline manganates *romanechite* (containing less iron and more water) from Romanèche, Frante, and *coronadite* (with high lead

and low barium contents) from Arizona. (L. L. Fermor, *The Manganese Ore Deposits of India*, Mem. Geol. Survey India, 1909, 37; Rec. Geol. Survey India, 1917, 48, 103.)

L. J. S.

HOLMES STILL (*v.* Vol. I, 346*c*).

**HOLMIUM.** Ho. At. no. 67. At. wt. 163.5. This element, which belongs to the yttrium group of the rare earth metals, was discovered spectroscopically by Cleve in 1879 in the terbia of C. G. Mosander or erbia of N. J. Berlin. Many years elapsed, however, before Holmberg (*Z. anorg. Chem.* 1911, 71, 226) was able to obtain sufficiently pure specimens of holmium salts to establish definitely the individuality of the element. From 29 kilos of euxenite he first separated the yttrium earths and then fractionally crystallised the *m*-nitrobenzenesulphonates; the head fractions containing Y, Ho, Dy, Tb, Gd, Eu and Sm were converted into the nitrates, bismuth nitrate added, and crystallisation continued to remove gadolinium. The oxalates were now fractionated, the most soluble fractions being further treated as nitrates. Final purification was by partial precipitation with aniline.

Driggs and Hopkins (*J. Amer. Chem. Soc.* 1925, 47, 363) found that the most persistent impurity in holmium was erbium which could be removed by crystallisation of the bromates. In this way it was possible to obtain fractions contaminated

only with yttrium, an impurity which could be eliminated fairly readily by partial decomposition of the nitrates; the course of the separation was followed by determining the magnetic susceptibility. Atomic weight determinations from the purest fractions of holmium chloride gave  $\text{Ho} = 163.47$ .

**Physical Properties.**—According to Aston (Proc. Roy. Soc. 1934, A, 148, 46) holmium is a single element possessing only one isotope,  $^{165}\text{Ho}$ , the mass-spectrum atomic weight being 164.91, a figure considerably higher than the best atomic weight determined chemically. Bartlett, Jr. (Physical Rev. 1934, [ii], 45, 847) has shown on theoretical grounds that the isotope  $^{163}\text{Ho}$  should be stable and, possibly, it still awaits detection.

The atomic magnetic moment of the holmium ion is probably  $13.689 \pm 0.06$ . The reduction potential and the potential of metal formation are, respectively,  $-1.790$  and  $-1.885$ .

**Spectra.**—The most prominent lines in the arc and spark spectra are: 3399.0, 3425.4, 3428.1, 3453.1, 3456.0, 3462.0, 3474.3, 3484.8, 3494.8, 3515.6, 3598.8, 3662.3, 3748.2, 3767.3, 3889.0, 3891.0, 4045.4, 4103.8, 4254.4 (King, Physical Rev. 1929, [ii], 33, 540; Astrophys. J. 1930, 72, 221).

Absorption spectra have been studied by Holmberg (Lc.), Yntema (J. Amer. Chem. Soc. 1923, 45, 907), Prandtl and Scheiner (Z. anorg. Chem. 1934, 220, 107) and Gobrecht (Physikal. Z. 1936, 37, 549).

**Compounds.**—Numerous salts of holmium have been made but, like those of many other rare earths, descriptions of them are meagre.

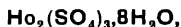
**Holmium Sesquioxide (Holmia),  $\text{Ho}_2\text{O}_3$ .**—Obtained as a yellow solid by igniting the hydroxide, nitrate, oxalate or sulphate; it dissolves in acids to form yellow-coloured holmium salts. For its magnetic properties, see Cabrera (Compt. rend. 1937, 205, 400), Trombe (Ann. Physique, 1937, [xi], 7, 385) and Velazos (Anal. Fis. Quim. 1935, 38, 297).

**Holmium Chloride,  $\text{HoCl}_3$ .**—Light-yellow crystalline solid, m.p.  $718^\circ\text{C}$ ., formed by heating the hydrated salt in a current of hydrogen chloride at  $350^\circ$ .

A similar method is employed for the preparation of the *bromide*, except that ammonium bromide is mixed with the hydrated salt and is then removed either by heating to  $600^\circ$ , or at  $350^\circ$  *in vacuo*. It melts at  $914^\circ$ .

The *iodide* is also a light-yellow solid, m.p.  $1,010 \pm 10^\circ$ , and is obtained by passing hydrogen iodide over the anhydrous chloride at  $600^\circ$  (Jantsch *et al.*, Z. anorg. Chem. 1932, 207, 353).

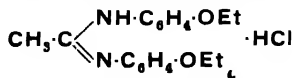
**Holmium Sulphate Octahydrate,**



has been made and its magnetic properties have been closely studied.

G. R. D.

"**HOLOCAINE**," syn. "*Phenocain*," di-(*p*-ethoxyphenyl)acetamidine hydrochloride,



finds application as a local anæsthetic in

ophthalmic surgery, but its more general use is restricted by its toxicity (G.P. 79868, 80568).

**HOLOKLASTIT** (v. Vol. IV, 464a).

"**HOMATROPINE**," tropine mandelic ester,  $\text{C}_8\text{H}_9\text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_5$ , is prepared by prolonged heating of tropine mandelate with dilute hydrochloric acid; the hydrochloride so produced is usually converted into the hydrobromide. It is used as a mydriatic which is less toxic than atropine; the mydriatic activity is still more marked when used with ephedrine (Pak and Tang, Proc. Soc. Exp. Biol. Med. 1930, 27, 887). Identification of homatropine: Ekert, Pharm. Zentralk. 1930, 71, 180; Celsi, Anal. Farm. Biochim. 1930, 1, 140. Microchemistry: Kofler and Müller, Mikrochem. 1937, 22, 43.

**HOMOCATECHOL**, homopyrocatechol, 3:4-dihydroxytoluene, m.p.  $65^\circ$ , b.p.  $251-252^\circ$ ; *creosol* is the 3-methyl ether, m.p.  $5-5^\circ$ , b.p.  $221-222^\circ$ ,  $d_4^{20}$  1.111.

**HOMOCHELIDONINE** (v. Vol. II, 527d)

**HOMOCOL** (v. Vol. III, 515b).

**HOMOEUNYSTEROL** (v. Vol. IV, 400c).

**HOMOGENEOUS CATALYSIS.**

#### SYNOPSIS OF THE SUBJECT.

- (a) Introduction (p. 240d).
- (b) Catalysis and the classical dissociation theory (p. 241d).
- (c) Salt effects in catalysed reactions (p. 213b).
- (d) Modern views on acids and bases (p. 247a).
- (e) General acid-base catalysis (p. 249b).
- (f) The use of catalytic measurements for determining hydrogen- and hydroxyl-ion concentrations (p. 251b).
- (g) Relations between catalytic power and acid-base strength (p. 252d).
- (h) The mechanism of acid-base catalysis (p. 255b).
- (i) Other types of positive catalysis in solution (p. 258b).
- (k) Negative catalysis in solution (p. 260c).

#### (a) INTRODUCTION.

The term *catalysis* in its modern sense was introduced by Berzelius in 1836 to describe a number of chemical phenomena in which one of the substances apparently responsible for the reaction (the catalyst) remains unchanged. The phenomena which he considered would now be divided into two classes, *heterogeneous catalysis* and *homogeneous catalysis*, according to whether the catalyst is present as a separate phase, or constitutes part of a homogeneous system. Of the two, heterogeneous catalysis has probably been the subject of more investigation, largely because of its practical importance in gas reactions (v. CATALYSIS IN INDUSTRIAL CHEMISTRY). On the other-hand, homogeneous catalysis in solution has been closely connected with the development of the modern theory of solutions, and is involved in many organic reactions of practical importance, notably esterification and hydrolytic reactions.

It has long been realised that the function of catalysts (both heterogeneous and homogeneous) is to modify the velocity of a reaction, without affecting the position of the equilibrium which is finally reached. In the case of homogeneous catalysis the relation between the amount of catalyst present and the reaction velocity usually has a simple form. For example, if a reaction  $A \rightarrow B$  is taking place under the effect

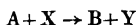


of a catalyst X, then its progress with time  $t$  will usually be governed by the equation

$$-\frac{d[A]}{dt} = k_X[X][A] \quad (1)$$

where the square brackets denote concentrations. For a given reaction the constant  $k_X$  depends upon the nature of the catalyst X, and on the temperature and the nature of the solvent: it is known as the *catalytic constant* and serves as a measure of the effectiveness of the catalyst under the given conditions.

Since  $[X]$  remains constant throughout the change, the course of a single reaction will be kinetically of the first order with a velocity constant  $k = k_X[X]$ : the catalysed reaction is thus of the same kinetic order as the uncatalysed reaction  $A \rightarrow B$ . On the other hand equation (1) is identical with that for a bimolecular reaction between X and A, except that the concentration of X remains constant during the reaction: i.e. instead of



where X is transformed into Y, we have



where X ultimately emerges unchanged from the reaction.  $k_X$  has in fact the dimensions of a bimolecular velocity constant, and the above reaction must be pictured (in spite of its first order kinetics) as depending on bimolecular collisions between A and X. Exactly similar considerations apply to reactions of higher order. For example, if the reaction  $A + B \rightarrow C + D$  is catalysed by X the kinetic equation will be

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_X[X][A][B] \quad (2)$$

and the reaction will follow a second order course with a velocity constant  $k_X[X]$ .

In the case of reversible reactions the law that the position of equilibrium is unaffected by a catalyst imposes some restrictions on the catalytic constants. For example, if the reaction  $A \rightleftharpoons B$  is catalysed by X the velocities in the two directions are given by

$$-\frac{d[A]}{dt} = k'_X[X][A], \quad -\frac{d[B]}{dt} = k''[X][B] \quad (3)$$

At equilibrium the velocities in the two directions must be equal, giving  $\frac{[B]}{[A]} = \frac{k'_X}{k''}$ : hence

the ratio  $\frac{k'_X}{k''}$  must be independent of the nature of X, though of course the separate values of  $k'$  and  $k''$  will depend upon X. Moreover, if the reaction proceeds under the same conditions of solvent and temperature in the absence of a catalyst, then the ratio of the uncatalysed velocity coefficients  $\frac{k'_0}{k''_0}$  must also

have the same value. These relations have been verified in a few cases, and can be regarded as firmly established on account of their thermodynamic basis. It should, however, be noted that they will only remain valid provided that

the concentration of the catalyst is not too high. A very large catalyst concentration will produce an appreciable change in the nature of the solvent medium, and may thus affect the position of equilibrium like any other change of solvent.

The types of reaction which are subject to homogeneous catalysis are very diverse, and no enumeration or classification will be attempted. On the other hand, most of the catalysts on which information is available fall into a few well-defined classes, as follows:—

(i) *Catalysis by Acids and Bases*.—This is by far the most extensive field in homogeneous catalysis, and a large part of this article will be devoted to various aspects of acid-base catalysis.

(ii) *Catalysis by Ions other than Acid or Basic Ions*.—There are a number of isolated instances of catalysis by metallic ions and halide ions, usually depending upon possibilities of alternate oxidation and reduction of the catalyst. These will be described in section (i).

(iii) *Catalysis of Organic Reactions by Inorganic Halogenides*.—This class of reaction, typified by the Friedel-Crafts reaction, is often carried out under heterogeneous conditions, but appears to be essentially homogeneous in character. A brief account is given in section (i).

(iv) *Catalysis by Enzymes*.—This may formally be treated as a type of homogeneous catalysis in solution, but the laws governing it are much more complex than for ordinary chemical catalysis (v. ENZYMES; FERMENTATION, ALCOHOLIC; HYDROLYSIS).

(v) *Negative Catalysis*.—This occurs both in gas reactions and in solution, and is a characteristic of chain reactions. Its occurrence in solution is dealt with in section (j).

#### (b) CATALYSIS AND THE CLASSICAL DISSOCIATION THEORY.

The early study of catalysis by acids and bases was closely connected with the development of the *electrolytic dissociation theory* towards the end of the nineteenth century, and this theory gained a good deal of support from measurements of reaction velocity. Thus both Ostwald and Arrhenius carried out such measurements, particularly on the *hydrolysis of esters* and the *inversion of cane sugar*, both of which are catalysed by acids. It was found that the catalytic power of a solution of an acid was directly proportional to its electrolytic conductivity for a large range of concentrations. This was interpreted by supposing that the hydrogen ion in solution was the only effective catalyst present, and that the hydrogen ion concentration was measured by the electrolytic conductivity.<sup>1</sup> Although according to modern views some qualifications must be attached to these statements (especially for certain other reactions), they still constitute a valuable working basis in many cases. Table I shows the figures given by Ostwald (J. pr. Chem. 1884, [ii]),

<sup>1</sup> The last statement is not strictly true even according to the simple dissociation theory, since that part of the conductivity depending on the anion will vary from one acid to another. However, owing to the very high mobility of the hydrogen ion little error is made in assuming that the conductivities of solutions of different acids are proportional to their hydrogen ion concentrations.

30, 93). All the data refer to *N* aqueous solutions of the acids, and the numbers represent relative values of their conductivity and of their catalytic effects in the hydrolysis of methyl acetate and the inversion of cane sugar, the value for hydrochloric acid being taken arbitrarily as 100 in each case.

TABLE I.—RELATIVE CONDUCTIVITIES AND CATALYTIC EFFECTS OF DIFFERENT ACIDS.

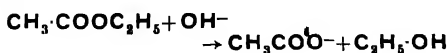
Acid	Con- duc- tivity.	<i>k</i> (ester).	<i>k</i> (sugar)
HCl	100	100	100
HBr	101	98	111
HNO <sub>3</sub>	99.6	92	100
H <sub>2</sub> SO <sub>4</sub>	65.1	73.9	73.2
CCl <sub>3</sub> COOH	62.3	68.2	75.4
CHCl <sub>2</sub> COOH	25.3	23.0	27.1
COOH.COOH	19.7	17.6	18.6
CH <sub>2</sub> Cl.COOH	4.90	4.30	4.84
H.COOH	1.68	1.31	1.53
CH <sub>3</sub> CH(OH)CO <sub>2</sub> H	1.04	0.90	1.07
CH <sub>3</sub> COOH	0.424	0.345	0.400
CH <sub>3</sub> CH(CH <sub>3</sub> )COOH	0.311	0.268	0.335

Similar conditions obtain in alcoholic solutions, though data are here less numerous. Table II (Goldschmidt, Ber. 1895, 28, 3218, and later papers) shows the parallelism between conductivity and catalytic effect for the esterification of formic acid in ethyl alcohol solution. The ethyl alcohol serves both as solvent and as reactant, and the hydrogen ions are provided by an added catalyst acid, formic acid being too weak to have any appreciable catalysing effect. The concentration of the catalysing acid was 0.10*N*. throughout.

TABLE II.—CATALYTIC EFFECT OF ACIDS IN THE ESTERIFICATION OF FORMIC ACID IN ETHYL ALCOHOL.

Catalysing acid.	Relative conductivity	Relative velocity constant
Hydrogen chloride.	100	100
Picric . . . . .	10.4	10.3
Trichloroacetic . .	1.00	1.04
Trichlorobutyric . .	0.35	0.30
Dichloroacetic . . .	0.22	0.18

An exactly analogous interpretation can be applied to catalysis by bases, i.e. the catalytic effect of a basic solution depends upon its hydroxyl ion concentration, which can be determined from its conductivity. Experimental data are, however, much less extensive than in the case of acid catalysis. Most of the early work was done on the hydrolysis of esters in presence of alkali, which cannot, strictly speaking, be classed as a catalytic reaction since hydroxyl ions are used up during the reaction, e.g.



It was found that in dilute solutions of sodium, potassium and calcium hydroxides (which may be regarded as completely dissociated) the rate of hydrolysis is proportional to the normality of the alkali and is independent of the nature of the catalysed reaction: further, solutions of the weak base ammonia give rise to much smaller velocities. Similar results have been obtained later with the reversible conversion of acetone into diacetone alcohol according to the equation



which is catalysed by solutions of strong and weak bases.

It is possible on the basis of the classical dissociation theory to make some general statements on the variation of reaction velocity with hydrogen ion concentration or with  $p_H$

$$(-\log_{10} [\text{H}^+]).$$

These statements apply strictly only to catalysis by dilute solutions of strong acids and bases, but for many reactions they serve also to give a general description of the behaviour in presence of weak electrolytes. Many reactions are catalysed both by acids and by bases, and the most general equation for the observed velocity constant *k* is

$$k = k_0 + (k_{\text{H}^+})[\text{H}^+] + (k_{\text{OH}^-})[\text{OH}^-] \quad (4)$$

where  $k_{\text{H}^+}$  is the catalytic constant of the hydrogen ion,  $k_{\text{OH}^-}$  the catalytic constant of the hydroxyl ion, and  $k_0$  the velocity constant of the so-called "spontaneous" reaction.<sup>1</sup>

The relative importance of the three terms in equation (4) varies very much under different conditions and for different reactions (cf. e.g. Skrabal, Z. Elektrochem. 1927, 33, 322). The application of the law of mass action to the dissociation of water gives  $[\text{OH}^-][\text{H}^+] = K_w$ , the ionic product of water, and insertion of this in equation (4) gives

$$k = k_0 + (k_{\text{H}^+})[\text{H}^+] + \frac{(k_{\text{OH}^-})K_w}{[\text{H}^+]} \\ = k_0 + \frac{(k_{\text{H}^+})K_w}{[\text{OH}^-]} + (k_{\text{OH}^-})[\text{OH}^-] \quad (5)$$

Since  $K_w \approx 10^{-14}$ ,  $[\text{H}^+]$  and  $[\text{OH}^-]$  vary by a factor of about  $10^{12}$  in passing from 0.10*N*. hydrochloric acid to 0.10*N*. sodium hydroxide, so that unless  $k_{\text{H}^+}$  and  $k_{\text{OH}^-}$  differ by a factor of more than about  $10^9$  there will be two ranges of  $p_H$  easily accessible to experiment in which one of the last two terms in equation (5) can be neglected. In these ranges the velocity is a linear function of  $[\text{H}^+]$  and  $[\text{OH}^-]$  respectively, and the values of the corresponding catalytic constants  $k_{\text{H}^+}$  and  $k_{\text{OH}^-}$  can easily be separately determined from the experiment. Between these two ranges the reaction velocity will pass through a minimum value of

$$k_{\text{min}} = k_0 + 2\sqrt{K_w(k_{\text{H}^+})(k_{\text{OH}^-})} \quad (6)$$

<sup>1</sup> It will be seen later that the term "spontaneous" is really a misnomer, since the observed velocity is actually due to catalysis by the solvent molecules. However, the term is in very general use and will be retained.

at a hydrogen ion concentration given by

$$[\text{H}^+]_{\text{min}} = \left\{ \frac{K_w(k_{\text{OH}^-})}{k_{\text{H}^+}} \right\}^{\frac{1}{2}} \quad (7)$$

If  $k_{\text{OH}^-} = k_{\text{H}^+}$  the minimum velocity will be at the neutral point, while the two possibilities  $k_{\text{OH}^-} > k_{\text{H}^+}$  and  $k_{\text{OH}^-} < k_{\text{H}^+}$  correspond to a minimum velocity respectively on the acid and on the alkaline side of the neutral point.

Under some conditions ( $k_0$  not too small,  $(k_{\text{H}^+})(k_{\text{OH}^-})$  not too large) the second term in equation (6) is negligible compared with the first, and the velocity at the minimum point is equal to the spontaneous velocity  $k_0$ . Moreover, reference to equation (5) shows that under the same conditions there will be an appreciable range of  $p_{\text{H}}$  values over which the two last terms of this equation contribute very little to the velocity. Under these conditions the spontaneous velocity  $k_0$  is directly observable as the measured velocity in this  $p_{\text{H}}$  range. When this is not the case the value of  $k_0$  must be obtained either from the observed minimum velocity by using equation (6), or by extrapolating the linear parts of the  $k$ - $[\text{H}^+]$  or  $k$ - $[\text{OH}^-]$  plots to zero concentration of  $[\text{H}^+]$  or  $[\text{OH}^-]$ . Finally, many reactions are of course known in which one or more of the constants  $k_0$ ,  $k_{\text{H}^+}$  and  $k_{\text{OH}^-}$  is zero, or at least so small that it cannot be detected.

The following list gives the different possible types of behaviour, with a few of the better known examples of each type:

(1) Catalysis by both acids and bases, spontaneous reaction directly observable. Example—the mutarotation of glucose.

(2) Catalysis by both acids and bases, spontaneous reaction detectable but not directly observable. Example—the halogenation of acetone.

(3) Catalysis by both acids and bases, spontaneous reaction not detectable. Examples—the hydrolysis of amides and  $\gamma$ -lactones.

(4) Catalysis by acids only, spontaneous reaction directly observable. Examples—the hydrolysis of alkyl orthoacetates and ortho-carbonates.

(5) Catalysis by bases only, spontaneous reaction directly observable. Examples—the hydrolysis of  $\beta$ -lactones, the decomposition of nitramide, the halogenation of nitro-paraffins.

(6) Catalysis by acids only, no spontaneous reaction detectable. Examples—the inversion of sugars, the hydrolysis of diazoacetic ester and of acetals.

(7) Catalysis by bases only, no spontaneous reaction detectable. Examples—the depolymerisation of diacetone alcohol, the decomposition of nitrosotriacetoneamine.

#### (c) SALT EFFECTS IN CATALYSED REACTIONS.

Although the classical theory gave a good general account of the experimental data, a number of discrepancies remained, of which the following are the most important:

(i) The reaction velocity is not exactly a linear function of the hydrogen or hydroxyl ion concentration as calculated from the con-

ductivity. In particular, in catalysis by solutions of strong acids an increase of acid concentration invariably causes the velocity to increase more rapidly than the conductivity.

(ii) The reaction velocity is often affected considerably by the addition of neutral salts, i.e. salts which are neither acidic nor basic and which have no ion in common with the catalyst. This discrepancy is particularly marked in solutions containing weak electrolytes.

(iii) The addition of a salt having an ion in common with the catalyst does not usually depress the velocity as much as would be expected from the simple law of mass action.

Subsequent work on the theory of acid-base catalysis has been largely devoted to clearing up these discrepancies, and the following are the chief modifications and additional assumptions which have been introduced into the classical theory:

(1) The ionic concentrations of strong electrolyte solutions are not proportional to their conductivities.

(2) The simple law of mass action does not apply exactly to ionic equilibria.

(3) The reaction velocity in ionic systems is not exactly a linear function of the concentrations of the reactants, but also depends on other properties of the solution, e.g. the concentrations of other ions present.

(4) Hydrogen and hydroxyl ions are not the only catalysing species.

Of these, (1), (2) and (3) are closely connected with modern electrolytic theory, and are treated in this section under the general description of "salt effects." (4) is the fundamental assumption of the theory of general acid-base catalysis, and forms the subject of the two following sections.

According to modern views (based partly on theoretical considerations and partly on experimental evidence) those electrolytes commonly classed as "strong" are, practically speaking, 100% dissociated even at concentrations where their conductivity ratios are considerably less than unity. The decrease of conductivity is attributed to electrostatic forces between the ions, and not to incomplete dissociation. This hypothesis of *complete dissociation of strong electrolytes* often introduces a considerable simplification into the treatment of catalytic data. This is illustrated by the data in Tables III and IV (p. 244) (cf. Dawson and Lowson, J.C.S. 1928, 2146; La Mer and Miller, J. Amer. Chem. Soc. 1935, 57, 2674; Koelichen, Z. physikal. Chem. 1900, 33, 129). The experiments of Koelichen were carried out at 25.2°, and his velocity constants have been reduced by 1.3% to make them comparable with those at 25°.

It will be seen that the catalytic constant  $\frac{k}{c}$  remains constant over a large range of concentrations provided that the catalyst is assumed to be completely dissociated, although the conductivity ratio  $\frac{\Lambda}{\Lambda_0}$  varies by 13–16% over the same concentration range. (The last column contains the activity coefficient  $f$  of the catalyst, and will be discussed later.) It should not be

TABLE III.—HYDROLYSIS OF ETHYL ACETATE AT 25°, CATALYST HCl.

 $k$ =first-order velocity constant, min.<sup>-1</sup>.

$c$ (HCl).	$\frac{k}{c}$	$\frac{\Lambda}{\Lambda_0}$	$f$ (HCl).
0.0002	6.43	0.999	0.993
0.0005	6.50	0.998	0.984
0.0010	6.50	0.997	0.965
0.0020	6.49	0.990	0.957
0.0100	6.54	0.984	0.924
0.0200	6.45	0.973	0.892
0.0400	6.50	0.952	0.860
0.1000	6.48	0.903	0.814
0.2000	6.57	0.895	0.783
0.5000	6.76	0.865	0.762

TABLE IV.—DECOMPOSITION OF DIACETONE ALCOHOL AT 25°, CATALYST NaOH.

 $k$ =first-order velocity constant, min.<sup>-1</sup>.

Author.	$c$ (NaOH).	$\frac{k}{c}$	$\frac{\Lambda}{\Lambda_0}$	$f$ (NaOH)
(1)	0.00471	2.20	0.970	0.936
(1)	0.00942	2.32	0.955	0.904
(1)	0.0188	2.29	0.901	0.865
(2)	0.0205	2.22	0.897	0.860
(2)	0.0292	2.23	0.885	0.838
(1)	0.0471	2.32	0.867	0.810
(2)	0.0518	2.24	0.861	0.804
(2)	0.0616	2.22	0.854	0.793
(2)	0.0710	2.22	0.848	0.782
(2)	0.0864	2.19	0.843	0.770
(1)	0.0942	2.28	0.840	0.766
(2)	0.1045	2.21	0.838	0.760

(1) Koelichen.

(2) La Mer and Miller.

assumed that the reaction velocity is always exactly proportional to the concentration of the catalyst ion, since deviations from such proportionality will be discussed a little later under the heading of primary salt effects. However, the velocity is always more nearly proportional to the concentration than to the conductivity. The position is similar in non-aqueous solvents, in fact the direct proportionality between catalyst concentration and reaction velocity found by Goldschmidt *et al.* (*ibid.* 1912, **81**, 30; 1920, **94**, 233) for esterification reactions in methyl and ethyl alcohols, constituted some of the most convincing evidence for complete dissociation in these solvents (*cf.* Bjerrum, *Fysisk Tidsskr.* 1916, **15**, 59; *Z. Elektrochem.* 1918, **24**, 321).

The most important deviations from the classical laws of catalysis occur when weak electrolytes are present, and these are now attributed to the *secondary salt effect* (Brönsted, *J.C.S.* 1921, **119**, 574; Brönsted and Pedersen, *Z. physikal. Chem.* 1924, **108**, 185). The term "secondary" refers to the fact that these effects are not primarily concerned with the reaction itself, but with the

ionic equilibria present. According to modern electrolyte theory these equilibria, and hence the concentrations of the catalysing ions, are affected to a considerable extent by the total ionic concentration of the solution. This is expressed in terms of *activity coefficients*; *e.g.* for the dissociation of a weak acid  $HA$  according to the equation  $HA \rightleftharpoons H^+ + A^-$  the simple mass action expression must be replaced by

$$\frac{[H^+][A^-]}{[HA]} \frac{(f_{H^+})(f_{A^-})}{f_{HA}} = K. \quad (8)$$

where  $K$  is the true or thermodynamic dissociation constant (depending only on the temperature and the solvent) and the  $f$ 's are activity coefficients. The "classical" concentration dissociation constant  $K_c$  is that given by

$$K_c = \frac{[H^+][A^-]}{[HA]} \frac{f_{HA}}{(f_{H^+})(f_{A^-})}. \quad (9)$$

The activity coefficients are all equal to unity at very low ionic concentrations, but as the concentration of ions increases  $f_{H^+}$  and  $f_{A^-}$  both decrease. Hence in fairly dilute solutions an increase of ionic concentration increases  $K_c$ , the degree of dissociation, and the velocity of any reaction catalysed by hydrogen ions. In more concentrated solutions a change in the reverse direction often takes place.

Apart from measurements of reaction velocity or theoretical considerations, there is abundant evidence from indicator and electrometric measurements for the increased dissociation caused by the addition of salt. Table V gives typical data obtained from electrometric measurements, which illustrate the magnitude of the effect (Larsson and Adell, *ibid.* 1931, **156**, 352).

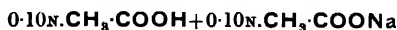
TABLE V.—CONCENTRATION DISSOCIATION CONSTANT OF ACETIC ACID IN SALT SOLUTIONS.

18°C.  $m$ =salt molality.

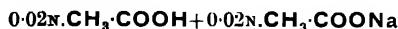
$m$ .	$10^5 K_c$ .	
	in KCl.	in $5rCl_2$ .
0	1.74	1.74
0.01	1.86	—
0.05	2.19	—
0.1	2.69	3.09
0.2	2.95	3.47
0.5	3.17	4.07
1.0	2.95	4.37
2.0	2.19	3.89

It is important to note that the ions formed by the dissociation of the weak electrolyte will contribute to these interionic effects in just the same way as the ions of an added salt. This factor is not important in a solution made directly by dissolving a weak electrolyte, since in these cases the ionic concentration is small. However, in a buffer solution, such as acetic acid plus sodium acetate, the acetate ions must be

taken into account in calculating the total salt concentration in spite of the fact that they also take part in the dissociation equilibrium. In consequence of this fact the hydrogen ion concentration of a buffer mixture does not remain quite constant when the solution is diluted, as would be predicted by the classical law of mass action: for example,  $[H^+]$  in



is greater than in



on account of the higher ionic concentration in the former solution.

The secondary salt effect is still more prominent in non-aqueous solutions, since on account of the lower dielectric constant the electrostatic forces are much greater than in water. In these solutions the ions formed by the weak electrolyte itself may produce a considerable effect, so that large deviations may occur even in unbuffered solutions of weak electrolytes without any salt additions. Typical data are given in the following table, containing data for the concentration dissociation constant of picric acid in ethyl alcohol measured by a colorimetric method (Gross and Goldstein, *Monatsh.* 1930, 55, 316). It will be seen that although the ionic concentration never exceeds 0.005*N.* the classical dissociation constant varies by a factor of more than 3.

TABLE VI.—DISSOCIATION OF PICRIC ACID IN ETHYL ALCOHOL AT 20°C.

$c_1$	$c_2$	$c_t$	$10^4 K_a$
0	0	0	1.84 (extrapolated)
$1.022 \times 10^{-5}$	0	$0.67 \times 10^{-6}$	1.94
$1.873 \times 10^{-5}$	0	$1.71 \times 10^{-6}$	1.96
$4.080 \times 10^{-5}$	0	$3.48 \times 10^{-6}$	2.00
$1.280 \times 10^{-4}$	0	$8.97 \times 10^{-6}$	2.13
$2.876 \times 10^{-4}$	0	$1.69 \times 10^{-5}$	2.28
$1.087 \times 10^{-3}$	0	$4.16 \times 10^{-5}$	2.58
$2.337 \times 10^{-4}$	$3.27 \times 10^{-4}$	$4.75 \times 10^{-4}$	2.60
$1.705 \times 10^{-3}$	0	$5.81 \times 10^{-5}$	2.75
$2.930 \times 10^{-4}$	$4.10 \times 10^{-4}$	$5.90 \times 10^{-4}$	2.76
$2.857 \times 10^{-3}$	0	$7.84 \times 10^{-5}$	3.01
$2.914 \times 10^{-4}$	$1.019 \times 10^{-3}$	$1.20 \times 10^{-3}$	3.32
$7.041 \times 10^{-3}$	0	$1.35 \times 10^{-3}$	3.24
$2.323 \times 10^{-4}$	$1.678 \times 10^{-3}$	$1.84 \times 10^{-3}$	3.02
$1.453 \times 10^{-3}$	$4.111 \times 10^{-3}$	$4.24 \times 10^{-3}$	6.21

$c_1$  = concentration of picric acid.

$c_2$  = concentration of added salt (lithium chloride).

$c_t$  = total ionic concentration.

The bearing of secondary salt effects on catalysed reactions was first realised by Brönsted, and most of the experimental work on this subject comes from his laboratory (e.g. Brönsted and Teeter, *J. Physical Chem.* 1924, 28, 579; Brönsted and King, *J. Amer. Chem. Soc.* 1925, 47, 2523; Kilpatrick, *ibid.* 1926, 48, 2091; Brönsted and Wynne-Jones, *Trans. Faraday Soc.* 1929, 25, 59). Table VII (Brönsted and Teeter, *l.c.*) illustrates the effect of adding a neutral salt to a weak acid. The third column shows the values of  $[H^+]$  calculated from the kinetic data, using the catalytic con-

stant obtained from dilute solutions of strong acids. The last column contains the corresponding calculated dissociation constants, which may be compared with those in Table V.

TABLE VII.—DECOMPOSITION OF DIAZOACETIC ESTER IN 0.05*M.* ACETIC ACID AT 15°.

$k$  = first-order velocity constant,  $\text{min.}^{-1}$ .

$[KNO_3]$	$10k$	$10^4[H^+]$	$10^4 K$
0	12.71	9.52	1.85
0.005	13.10	9.77	1.95
0.01	13.45	10.07	2.07
0.02	13.70	10.27	2.15
0.05	14.19	10.62	2.30
0.10	14.58	10.90	2.44

The secondary salt effect in buffer solutions is illustrated by Table VIII, which gives data for the acid-catalysed hydrolysis of ethylacetal (Brönsted and Wynne-Jones, *l.c.*). Although the buffer ratio is constant throughout there is a steady rise in velocity in the first five experiments, due to the increase of salt concentration and the resulting increase in the dissociation constant of formic acid. On the other hand, the last four experiments, in which the total salt concentration has been kept constant by the addition of the requisite amounts of sodium chloride, show an almost constant velocity. This device of adding a neutral salt to keep the total salt concentration constant is frequently used to eliminate the secondary salt effect and thus to simplify the interpretation of experimental results. It can, however, only be applied successfully in fairly dilute solutions, since above a salt concentration of 0.1–0.2*N.* (in aqueous solutions) individual differences between the effects of different salts begin to become

TABLE VIII.—HYDROLYSIS OF ACETAL IN FORMATE BUFFERS AT 20°.

Formic acid : formate = 2.96 throughout.  
 $k$  = first-order velocity constant,  $\text{min.}^{-1}$ .

[Formic acid]	[Formate]	[NaCl]	Ionic strength	$10^3 k$
0.0296	0.0100	—	0.011	12.5
0.0592	0.0200	—	0.020	13.4
0.1480	0.0500	—	0.050	15.1
0.2220	0.0750	—	0.075	16.4
0.2960	0.1000	—	0.100	17.8
0.1776	0.0600	0.0400	0.100	17.6
0.0987	0.0333	0.0667	0.100	17.7
0.0222	0.0075	0.0925	0.100	18.2

The interionic attraction theory of electrolytes leads to a theoretical expression for the activity coefficients in equations (8) and (9), thus providing a theoretical basis for the secondary salt effect and making it possible to predict its sign and approximate magnitude.

The *Debye-Hückel limiting law* for the activity coefficient  $f_i$  of an ion of charge  $z_i$  is

$$-\log_{10} f_i = Az_i^2 \sqrt{\mu} \quad (10)$$

$\mu$ , the ionic strength, is defined by

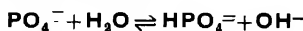
$$\mu = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} \sum c_i z_i^2 \quad (11)$$

where  $m_i$  and  $c_i$  are respectively the molality and equivalent concentration of an ion of species  $i$ , and the summation is made over all the ions present in the solution, including the ion whose activity coefficient is required. The constant  $A$  is given by the theory in terms of the temperature and properties of the solvent: for aqueous solutions at ordinary temperatures it is approximately equal to 0.5. In order to apply the theory to the dissociation of a weak electrolyte the values of the activity coefficients must be substituted in equation (9), giving

$$\log_{10} K_c = \log_{10} K + 2A\sqrt{\mu} \quad (12)$$

This equation predicts that the concentration dissociation constant will increase with increasing ionic strength, as illustrated in Tables V-VIII. However, both theory and practice indicate that equation (10) (and hence other equations derived from it) will only be valid for extremely dilute solutions, say up to about  $\mu = 0.01$  in water, and for most work on catalysis it will therefore only serve as a rough guide to the magnitude of the effect. It does, however, predict one notable feature of the secondary salt effect, namely that if the reaction velocity is plotted against  $\mu$  (or the concentration of added salt) the resulting curve is strongly concave to the concentration axis.

The above considerations apply to solutions in which the hydrogen ion concentration is determined by an equilibrium of the type  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ . Other types of equilibrium are possible: e.g. in a solution of an ammonium salt we have  $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ , and in a solution of a disulphate  $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$ . The effect of salt concentration can be predicted qualitatively by again using equations (9) and (10), taking into account the different charges on the species present. It is found that in the former case the hydrogen ion concentration should be unaffected by salt concentration, while in the latter case it should be increased. These predictions are borne out by the experimental results. The position is similar in reactions which are catalysed by the hydroxyl ion. In solutions of ammonia or an amine the relevant equilibrium is  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ , and the hydroxyl ion concentration is increased by addition of salt. On the other hand, in a buffer solution containing secondary and tertiary phosphate the equilibrium is



and theory predicts a decrease of hydroxyl ion concentration on the addition of salt, which is in fact the observed effect (Brønsted and King, *J. Amer. Chem. Soc.* 1925, **47**, 2523).

Catalysis in solution may be also subject to the *primary salt effect*, though this is normally of less importance than the secondary effect. As

the name "primary" implies, this effect operates directly on the velocity constant of the reaction, and is not concerned with displacements of the equilibria of weak electrolytes. It is therefore best studied in solutions containing only strong electrolytes, and has been the subject of a large mass of experimental work. (For references, see Bell, "Acid-Base Catalysis," Oxford, 1941, p. 23.) The following generalisations emerge from this work:

(a) For a given reaction and a given added salt the percentage change in velocity is a linear function of the salt concentration. This law appears to hold almost universally up to about 0.2N, and is often valid up to much higher concentrations.

(b) The magnitude of the effect depends upon the individual nature of the reaction and of the added salt, there being no general relation to the ionic strength.

(c) The addition of salt invariably causes an increase of velocity (positive salt effect) in reactions catalysed by hydrogen ions, while for hydroxyl ion catalysis the effect is sometimes positive and sometimes negative.

(d) When the hydrogen ion is the catalyst the specific effect of an added salt depends chiefly on the nature of its anion, while for hydroxyl ion catalysis the nature of the cation is the more important factor.

(e) The magnitude of the effect rarely exceeds 4-5% in 0.10N, aqueous solutions of uni-univalent salts, though in a few cases it may be as high as 10-12%.

The principle of the primary salt effect is now understood from a theoretical point of view (cf. Brønsted, *Z. physikal. Chem.* 1922, **102**, 169; 1925, **115**, 337; La Mer, *Chem. Reviews*, 1932, **10**, 179). However, the most interesting predictions of the theory relate to reactions involving two ions, and for a reaction involving an ion and a neutral molecule (as do the majority of catalysed reactions) the theory only predicts that the effect will be a linear one (cf. (a) above), without giving either its sign or its magnitude. The theory is therefore not described here. An interesting correlation between indicator measurements and primary salt effects in acid solutions has been demonstrated by Hammett and Deyrup (*J. Amer. Chem. Soc.* 1932, **54**, 2721) and Hammett and Paul (*ibid.* 1934, **56**, 830): this correlation has some theoretical basis and is certainly useful as a guide in practice.

It may be useful to summarise briefly the chief practical consequences of primary and secondary salt effects in catalysed reactions, with some mention of how the complications thus caused may be avoided.

(i) In solutions containing a weak electrolyte the reaction velocity will be affected by changes in the total salt concentration, whether these are brought about by adding a neutral salt or by changing the total concentration of a buffer solution.

(ii) In a solution of an ordinary weak acid (e.g. acetic acid), or a buffer solution prepared from it, the reaction velocity is increased by the addition of salt. An increase in salt concentration from zero to 0.10N, usually increases the velocity by 15-20% in a solution containing

only a weak acid, and 30–40% in a buffer solution.

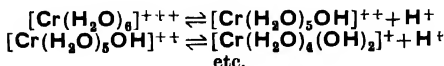
(iii) Complications due to this secondary salt effect can be largely eliminated in a series of experiments by maintaining a constant total salt concentration (not greater than  $N/5$ ) by adding the necessary quantities of neutral salt.

(iv) The primary salt effect modifies the velocity even when no weak electrolytes are present. It can frequently be neglected if the total salt concentration is not allowed to exceed  $N/10$ .

#### (d) MODERN VIEWS ON ACIDS AND BASES.

The understanding of acid-base catalysis has been closely connected with the development of ideas on the nature of acids and bases and the measurement of their strengths. It is therefore necessary to give some account of these ideas before describing further work on catalysis.

The Definition of an Acid has undergone a number of changes during the last fifty years. As soon as the ionic theory had become established an acid was defined as a substance containing hydrogen which gave rise to hydrogen ions in solution. Although acids were originally regarded as neutral molecules (like hydrogen chloride and acetic acid), it was soon found convenient to include negative ions such as  $\text{HSO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$ , which can also produce hydrogen ions in solution. These *anion acids* can of course only exist in practice in company with ions of opposite sign, and it might be suggested that salts like  $\text{NaHSO}_4$ ,  $\text{KH}_2\text{PO}_4$  should be regarded as acids. However, the sodium or potassium ions play no part in the acidic reactions of the salts, remaining unchanged throughout, and it is more logical to include only the anions in the definition. The modern definition of acids includes also *cation acids*: thus the acid character of solutions of ammonium salts is most simply explained as being due to the reaction  $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ , and the ammonium ion can therefore be considered as an acid. (The older description of the "hydrolysis" of ammonium chloride solution in terms of the two reactions  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$  and  $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$  is only a more cumbersome way of expressing the same facts, since the chloride ion plays no part in the process.) In the same way the acid properties of solutions of many metallic salts (*e.g.* iron, aluminium, chromium, etc.) are best explained by the splitting off of hydrogen ions from the hydrated cations, sometimes in several steps, *e.g.*



These hydrated ions can therefore be regarded as cation acids in the same way as the ammonium ion.

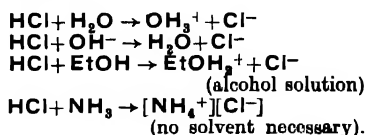
The Nature of the Hydrogen Ion in Solution has a considerable bearing on the definition of an acid. It was originally supposed to be simply a proton, the small size of which might serve to account for its high mobility, and possibly also for its catalytic power. However, there is now an overwhelming weight of

both experimental and theoretical evidence to show that the hydrogen ion in solution is invariably solvated, and that no measurable concentration of free protons can be present. In particular, it is believed that the hydrogen ion in aqueous solution exists entirely as  $\text{OH}_3^+$  (the oxonium or hydroxonium ion), which has a normal electronic structure with a completed octet and is analogous to the ammonium ion  $\text{NH}_4^+$ . In consequence all equations representing the production of a hydrogen ion in water should be rewritten so as to show the part played by the solvent, *e.g.* the dissociation of hydrogen chloride becomes

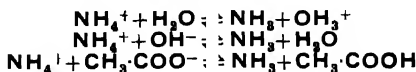


However, it is still common practice to use the symbol  $\text{H}^+$  for the hydrogen ion in solution, its solvation being tacitly assumed. It is clear that the nature of the hydrogen ion will actually vary from one solvent to another, *e.g.* in an alcohol  $\text{ROH}$  it has the formula  $\text{ROH}_2^+$ .

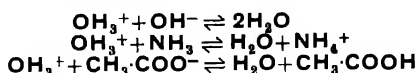
The term "hydrogen ion" which has been so far used in defining an acid is thus a somewhat ambiguous one. If it is taken to mean the actual species present in solution, the definition will vary from one solvent to another, while if it is taken to mean a free proton the definition is meaningless, since the production of this kind of "hydrogen ion" never takes place in practice. These difficulties are avoided by the modern definition, which reads: *An acid is a species having a tendency to lose a proton* (Bronsted, *Rec. trav. chim.* 1923, 42, 718; Lowry, *Chem. and Ind.* 1923, 1, 43). Although the production of a free proton is not possible, the tendency of the acid can be realised if some other species is present to receive the proton, and in the production of a solvated hydrogen ion the solvent acts as a proton acceptor. For example, all the following typically acidic reactions of hydrogen chloride involve the loss of a proton to another molecule or ion:



In exactly the same way the characteristic acid reactions of the ammonium ion involve the loss of a proton to give the ammonia molecule, *e.g.*

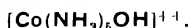


One important consequence of the above definition is that the oxonium ion  $\text{OH}_3^+$  must itself be regarded as an acid, its tendency to lose a proton being illustrated, for example, by the following reactions:

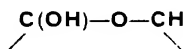


It will be seen that there is a close similarity between the oxonium and ammonium ions. In

results of Brønsted and Pedersen (*l.c.*) for acetate buffers. It will be seen that the increase of velocity is directly proportional to the acetate ion concentration, and independent of the  $p_H$  of the solution (determined by the buffer ratio). These results demonstrate conclusively basic catalysis by the acetate ion and make it possible to determine its catalytic constant with accuracy. Similar results were obtained with many other anion bases (both singly and doubly charged), with uncharged bases like aniline, and with positively charged bases of the type



The Mutarotation of Glucose has long been known to be catalysed both by acids and by bases, and played an important part in establishing the theory of general acid-base catalysis (Brønsted and Guggenheim, *ibid.* 1927, 49, 2554; Lowry and Smith, J.C.S. 1927, 2539; Westheimer, J. Org. Chem. 1938, 2, 431). The process observed is the interconversion of the isomers  $\alpha$ - and  $\beta$ -glucose, involving the rupture of a semi-acetal link



The catalytic effect of hydroxyl ions is about  $4 \times 10^4$  greater than that of hydrogen ions, and there is a considerable range of hydrogen ion concentrations (about  $p_H$  4-6) over which catalysis by both  $\text{OH}^-$  and  $\text{OH}_3^+$  can be neglected, enabling the "spontaneous" rate to be observed directly. The presence of general catalysis both by acids and by bases is most readily detected by using buffer solutions in this range, and experiment has shown that 43 other species are effective as catalysts, in addition to  $\text{OH}_3^+$  and  $\text{OH}^-$ , comprising the following types:

- Uncharged acids, e.g.  $\text{CH}_3\text{COOH}$ .
- Cation acids, e.g.  $\text{NH}_4^+$ .
- Uncharged bases, e.g.  $\text{NH}_3$ .
- Anion bases, e.g.  $\text{CH}_3\text{COO}^-$ ,  $\text{SO}_4^{=}$ .
- Cation bases, e.g.  $[\text{Co}(\text{NH}_3)_5\text{OH}]^{+1}$ .
- Amino-acids in the zwitterion form, e.g.



The effect of this last type of catalyst is due primarily to the basic properties of the group  $\text{COO}^-$ .

Fig. 1 shows data obtained by Brønsted and Guggenheim (J. Amer. Chem. Soc. 1927, 49, 2571) for sodium salts of various weak acids, a small quantity of the corresponding acid being added to bring the hydrogen ion concentration into the range  $10^{-6}$  to  $10^{-4}$ . (These amounts were insufficient to cause any appreciable acid catalysis.) It will be seen that the velocity is in each case a linear function of the anion concentration.

The Halogenation of Acetone was the first reaction for which catalysis by undissociated acid molecules was definitely established, and constitutes the only piece of evidence brought forward in support of the dual theory which has not been refuted by more modern work. The bulk of the work on this reaction is due to

Dawson *et al.* (numerous papers in J.C.S. 1913-29). Much of this was carried out before the importance of primary and secondary salt effects was realised, and the results are therefore often difficult to interpret. However, the general features of the reaction are clear, and have been confirmed by recent work (Smith, *ibid.* 1934, 1744; Lidwell and Bell, Proc. Roy. Soc. 1940, A, 176, 88). The reaction velocity is independent of the concentration of the halogen, and is the same for bromine and for iodine: hence the process of which the rate is measured precedes the halogenation and involves only the acetone molecule and the catalyst. (Modern views on the nature of this process are mentioned in section (g).) There is catalysis both by acids and by bases, hydroxyl ion being a much more powerful catalyst than hydrogen ion. The relative values for catalytic constants for  $\text{OH}^-$ ,  $\text{OH}_3^+$  and the spontaneous reaction are such that there is no appreciable range of hydrogen ion concentrations over which catalysis by both  $\text{OH}^-$  and  $\text{OH}_3^+$  can be neglected. This means that the spontaneous rate cannot be observed

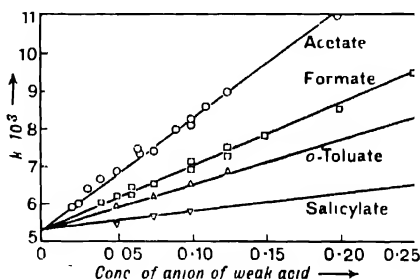


FIG. 1.

directly, and complicates the separation of the catalytic effects of different species. For example, in a solution containing a weak acid  $\text{HX}$  and its sodium salt the measured velocity  $k$  is equal to

$$k_0 + (k_H +) [\text{H}^+] + (k_{\text{OH}} -) [\text{OH}^-] + k_{\text{HX}} [\text{HX}] + (k_{\text{X}^-} -) [\text{X}^-]$$

where at the most one term (the second or third) can be neglected. A large number of carefully planned experiments is therefore necessary in order to determine the values of the individual catalytic constants.

Many other reactions are known which exhibit general acid-base catalysis in aqueous solution, of which the following may be mentioned: the bromination of substituted ketones and of ketonic esters (Pedersen, J. Physical Chem. 1933, 37, 751; 1934, 38, 601; Lidwell and Bell, Proc. Roy. Soc. 1940, A, 176, 88), the bromination of nitromethane (Pedersen, Kgl. Danske Vid. Selsk. Math.-fys. Medd. 1932, 12, 1), the hydrolysis of ortho-esters (Brønsted and Wynne-Jones, Trans. Faraday Soc. 1929, 25, 59), the decomposition of the diazoacetate ion (King and Bolinger, J. Amer. Chem. Soc. 1936, 58, 1533), the depolymerisation of dimeric dihydroxyacetone (Bell and Baughan, J.C.S. 1937, 1947), the oxidation of phosphorous and hypophosphorous



acids by iodine (Nylén, Z. anorg. Chem. 1937, 230, 385; Griffith, McKeown and Taylor, Trans. Faraday Soc. 1940, 36, 752), the formation and hydrolysis of semicarbazones (Conant and Bartlett, J. Amer. Chem. Soc. 1932, 54, 2881; Westheimer, *ibid.* 1934, 56, 1962).

The theory of general acid-base catalysis puts a new interpretation upon the "spontaneous" reaction, i.e. that part of the reaction velocity which is independent of the concentration of dissolved catalysts. It is now supposed that this reaction is not truly spontaneous (though the term is still frequently used for convenience), but is due to acid or basic catalysis by the water molecules, which can act either as acids or as bases. Although the acid or basic strength of the  $\text{H}_2\text{O}$  molecule is very small, it is present in very high concentrations, and therefore its catalytic effect may well be appreciable. There are two pieces of evidence which favour this interpretation. In the first place, all those reactions which exhibit general catalysis by acids or by bases also exhibit a measurable spontaneous reaction; conversely, those reactions which appear to be catalysed specifically by hydrogen or hydroxyl ions do not exhibit any measurable spontaneous reaction. In the second place, no spontaneous reaction can be detected in solvents which do not exhibit acidic or basic properties: e.g. nitramide is quite stable in chloroform solution, and tetramethylglucose undergoes no change in carefully purified hydrocarbon solvents.

The study of catalysis by acids and bases in non-aqueous solvents throws an interesting light on general catalysis. In other hydroxylic solvents the condition is similar to that in water, except that quantitative interpretation is more difficult on account of the paucity of information about the behaviour of electrolytes in these solvents, and the increased importance of inter-ionic effects. However, in inert solvents of the hydrocarbon type the position is very different. No free ions are formed in these solvents and, in particular, there are no analogues to the hydrogen or hydroxyl ions, since the solvent molecule is unable to pick up a proton or to split one off. Any catalytic behaviour observed in this type of solvent must therefore be due to the molecules of the added acid or base, since there are no other catalysts present. A number of reactions have been shown to exhibit general acid-base catalysis in benzene and similar solvents, though more work is needed to clear up certain complications which arise in this type of medium (Bell and co-workers, J.C.S. 1936-41; summary given by Bell, Trans. Faraday Soc. 1938, 34, 229).

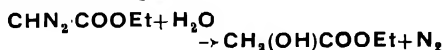
#### (f) THE USE OF CATALYTIC MEASUREMENTS FOR DETERMINING HYDROGEN- AND HYDROXYL-ION CONCENTRATIONS.

Measurements of the velocity of a catalysed reaction have long been used as a method for determining the concentration of hydrogen or hydroxyl ions in a solution. According to the classical theory this determination is a very direct one, since the velocity is supposed to be a simple linear function of  $[\text{OH}_3^+]$  or  $[\text{OH}^-]$ .

Later developments introduce some complications into this view. Thus it is obvious that reaction exhibiting general acid or base catalysis is unsuitable for this purpose, since the observed reaction velocity will depend not only on the concentration of  $\text{OH}_3^+$  or  $\text{OH}^-$ , but also on the concentrations of other acid or basic species present in the solution. Fortunately there are a number of reactions which appear to exhibit specific catalysis by hydrogen or hydroxyl ions, and the most useful of these will be described in this section. In another respect the modern theory has simplified the interpretation of the measured velocity, since it is now believed that the velocity is closely proportional to the concentration of the catalyst, and not (as has often been supposed) to its activity. This is illustrated by the data already given in Tables III and IV. In some cases it will be necessary to take into account the primary salt effect, but this is frequently small, and can be allowed for or minimised by keeping the salt concentration low.

#### The Decomposition of Diazoacetic Ester.

—In acid aqueous solution the following reaction takes place:



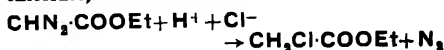
and can be conveniently followed by measuring the pressure or volume of the evolved nitrogen. It has been shown (Bredig and Fraenkel, Z. Elektrochem. 1905, 11, 525; Fraenkel, Z. physikal. Chem. 1907, 60, 202; Spitalsky, Z. anorg. Chem. 1907, 54, 278) that the velocity is proportional to the hydrogen ion concentration in solutions of both strong and weak acids. Examples of the results obtained are given in Table X.

TABLE X.—DECOMPOSITION OF DIAZOACETIC ESTER IN AQUEOUS SOLUTION (20°).

$k$  = first-order constant, min.<sup>-1</sup>.

Catalyst.	$10^4[\text{OH}_3^+]$ .	$10^4k$ .	$\frac{k}{[\text{OH}_3^+]}$
0.000900N. $\text{HNO}_3$ .	9.00	345	38.0
0.00182N. $\text{HNO}_3$ .	18.2	703	38.7
0.000364N. picric acid	3.64	140	38.3
0.000900N. picric acid	9.00	355	39.1
0.00900N. <i>m</i> -nitrobenzoic acid	10.8	432	37.6
0.0182N. acetic acid	5.63	218	38.8

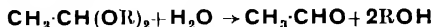
Measurements in buffer solutions agree with the assumption that the hydrogen ion is the only effective catalyst, provided that secondary salt effects are taken into account (*cf.* Table VII). There is also an unusually large primary salt effect, and a further complication arises from the fact that in the presence of many anions a second reaction takes place simultaneously, e.g. with chlorides,



This type of reaction has been found to take place in solutions of chlorides, nitrates and sulphates, but not of perchlorates and picrates.

In spite of these complications the diazoacetic ester reaction has been successfully used for the measurement of hydrogen ion concentrations, and hence of dissociation constants (*cf.* Brønsted *et al.*, *Z. physikal. Chem.* 1925, **117**, 299; 1927, **180**, 699; 1928, **134**, 97).

**The Hydrolysis of Acetals.**—These reactions are of the type

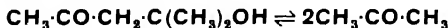


and are catalysed by acids but not by bases. They are more suited to the measurement of hydrogen ion concentrations than the hydrolysis of carboxylic esters, since these latter reactions produce acid, which interferes with the system under investigation. A large number of different acetals have been investigated by Skrabal by a chemical method. (For summary and references, see Skrabal, *Z. Elektrochem.* 1927, **33**, 322.) The possibility of catalysis by undissociated acid molecules was carefully investigated by Brønsted and co-workers using an accurate and convenient dilatometric method (Brønsted and Wynne-Jones, *Trans. Faraday Soc.* 1929, **25**, 59; Brønsted and Grove, *J. Amer. Chem. Soc.* 1930, **52**, 1394). They found that no such effect is detectable, and that there is no measurable "spontaneous" reaction. The first point is illustrated by the last four rows in Table VIII, where a change in the concentration of formic acid from 0.02*N.* to 0.3*N.* has no effect on the reaction velocity when the buffer ratio and the ionic strength are kept constant. The reaction velocity is thus directly proportional to the hydrogen ion concentration without any complications, and by a suitable choice of acetal a wide range of concentrations can be covered. Thus if *k* is the first order velocity constant at 26° (min.<sup>-1</sup>) and *c* the hydrogen ion concentration, we have the following values of *k/c*:

Ethylacetal	19
Methylacetal	3.92
Ethyleneacetal	0.180

The primary salt effect is fairly large, but has been extensively studied (Brønsted and Grove, *loc. cit.*).

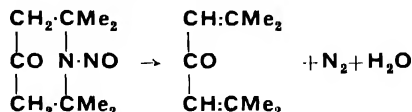
**The Decomposition of Diacetone Alcohol.**—This is a reversible reaction,



which, however, goes practically to completion in dilute aqueous solutions. It is catalysed by bases, but not by acids, and is accompanied by a large volume change so that its velocity can conveniently be followed by a dilatometric method. Data have already been given in Table IV to show the direct proportionality between reaction velocity and hydroxyl ion concentration in solutions of NaOH. (For other data, see French, *ibid.*, 1929, **51**, 3215; Murphy, *ibid.* 1931, **53**, 977.) An exhaustive study has been made of the primary salt effect in this reaction (Åkerlöf, *ibid.* 1926, **48**, 3046; 1927, **49**, 2955; 1928, **50**, 1272). There is no catalysis by water molecules or by the anions of weak acids, but primary and secondary (though not tertiary) amines do exert a catalytic effect, and therefore the reaction cannot be used for determining hydroxyl ion

concentrations in solutions containing these molecules. It is believed that this catalysis by amines is due to a specific chemical mechanism, and cannot be described as general basic catalysis (Miller and Kilpatrick, *ibid.* 1931, **53**, 3217; Westheimer and Cohen, *ibid.* 1938, **60**, 90; Ann. New York Acad. Sci. 1940, **39**, 401; Westheimer and Jones, *J. Amer. Chem. Soc.* 1941, **63**, 3283).

**The Decomposition of Nitrosotriacetone-amine.**—This is a first order reaction taking place according to the equation



and its velocity can be conveniently studied by measuring the pressure or volume of nitrogen evolved (Chubbens and Francis, *J.C.S.* 1912, **101**, 2358; Francis and Geake, *ibid.* 1913, **103**, 1722; Francis, Geake and Roche, *ibid.* 1915, **107**, 1651; Brønsted and King, *J. Amer. Chem. Soc.* 1925, **47**, 2523). The reaction velocity is directly proportional to the hydroxyl ion concentration up to about 0.5*N.*, above which concentration the reaction appears to be more complex. There is no evidence of general base catalysis, though no investigations have been specifically directed to this point.

The above four reactions are probably the most convenient for measuring hydrogen or hydroxyl ion concentrations. It should, however, be mentioned that for most purposes the *inversion of sucrose* and the *acid hydrolysis of carboxylic esters*, both in aqueous solution, can be regarded as examples of specific catalysis by hydrogen ions. It is a matter of some dispute how far undissociated acid molecules can exert a catalytic effect, but from a practical point of view such effects are certainly very small.

#### (g) RELATIONS BETWEEN CATALYTIC POWER AND ACID-BASE STRENGTH.

If the catalytic effects of several acid species for a given reaction can be compared, it is natural to expect that they will bear some relation to the acid strengths of the various species, in the sense that the stronger acid will be the more effective catalyst. It has in fact been found that this parallelism is a quantitative one, and it is usually referred to as the *Brønsted relation*, since it was first formulated by Brønsted and Pedersen in 1924 as a result of their work on the decomposition of nitramide (*Z. physikal. Chem.* 1924, **108**, 185). The relation can be written in the form

$$k_A = G_A K_A^\alpha, \text{ or } \log k_A = \log G_A + \alpha \log K_A. \quad (19)$$

where *k<sub>A</sub>* is the catalytic constant of a given acid catalyst, *K<sub>A</sub>* its dissociation constant, and *G<sub>A</sub>* and *α* are constant for a given reaction, solvent, temperature and series of similar catalysts. The constant *α* is always positive and less than unity. An exactly analogous equation holds for basic catalysis, *i.e.*

$$k_B = G_B K_B^\beta, \text{ or } \log k_B = \log G_B + \beta \log K_B. \quad (20)$$

$K_B$  is here the ordinary basic dissociation constant of the catalyst as defined in equation (18). It is however convenient for many purposes to express the basic strength of the catalyst by means of the reciprocal of the acid strength of the corresponding acid. As shown in section (d), this will not alter the form of equation (20) or the value of the constant  $\beta$ , though the value of  $G_B$  will be changed, and the equation can therefore be written

$$k_B = G'_B \left( \frac{1}{K_A} \right)^\beta, \text{ or } \log k_B = \log G'_B - \beta \log K_A \quad (2)$$

The Brönsted relation is analogous to several other relations which have been found to exist between reaction velocities and equilibrium constants, and some progress has been made towards a molecular interpretation of such regularities (*cf. e.g.* Hammett, *Chem. Reviews*, 1935, **17**, 125; *Trans. Faraday Soc.* 1938, **34**, 156; Horiuti and Polanyi, *Acta Physicochim. U.R.S.S.* 1935, **2**, 505; Bell, *Proc. Roy. Soc.* 1936, A, **154**, 414). However, there is no strict theoretical basis for these relations, and their accuracy or range of validity can only be determined by appeal to experiment. Actually the Brönsted relation has been found to hold without systematic deviations in all the reactions for which general acid base catalysis has been established, though the closeness with which it is obeyed varies somewhat from case to case. In the exact application of this relation to the experimental data it is necessary to take into account the so-called *statistical effect*, depending upon the number of points in the catalyst molecule at which a proton can be lost or picked up. However, the application of this correction rarely has much effect on the degree of agreement with the Brönsted relation, and in any case the way in which it should be applied in particular cases is often a matter of dispute, and is not discussed here (*cf.* Brönsted and Pedersen, *Z. physikal. Chem.* 1924, **103**, 185; Brönsted, *Chem. Reviews*, 1928, **5**, 322; Pedersen, *J. Physical Chem.* 1934, **38**, 581; *Trans. Faraday Soc.* 1938, **34**, 237; Westheimer, *J. Org. Chem.* 1938, **2**, 431).

Typical examples of the validity of the Brönsted relation are shown in Figs. 2 and 3, in which the symbols  $p$  and  $q$  refer to the *statistical effect* mentioned above (*cf.* section e, pp. 249c and 250a).

In each case the logarithm of the catalytic constant is plotted as ordinate against the logarithm of the dissociation constant of the corresponding acid as abscissa: *cf.* equation (21). For the decomposition of nitramide (Fig. 2) the points lie well on four straight lines, one corresponding to each class of bases investigated. The concordance is good, and usually within the limits of the experimental error.

For the mutarotation of glucose the agreement is not so good for any one class of catalyst, with the result that any differences between the classes as a whole are masked. As will be seen from Fig. 3, the data for a very varied selection of catalysts can be represented with moderate accuracy by a single relationship. There are no other reactions which have been investigated

in such detail as the two illustrated above, but the available data indicate similar behaviour for both acid- and base-catalysed reactions in many other cases.

Catalysis by the Hydrogen Ion, the Hydroxyl Ion and the Water Molecule should in principle be governed by the Brönsted relation. It is not, however, easy to test this, since there is some difficulty in giving a satisfactory numerical measure of the acid-base strengths of the species  $\text{OH}_3^+$ ,  $\text{OH}^-$  and  $\text{H}_2\text{O}$ . By formal analogy with the usual expression for the dissociation constant of an acid  $\text{HX}$ , *i.e.*

$$K_A = \frac{[\text{OH}_3^+][\text{X}^-]}{[\text{HX}]}$$

we can write

$$K_A(\text{H}_2\text{O}) = \frac{[\text{OH}_3^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{K_w}{55.5} \begin{cases} 1.07 \times 10^{-16} \text{ at } 18^\circ \\ 1.79 \times 10^{-16} \text{ at } 25^\circ \end{cases}$$

where 55.5 is the number of gram-molecules of  $\text{H}_2\text{O}$  in a litre of water. Similarly, the formal

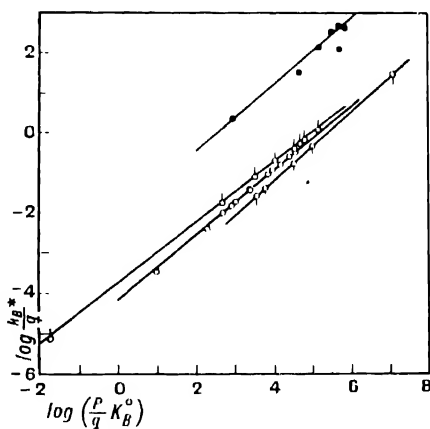
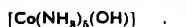


FIG. 2.—THE DECOMPOSITION OF NITRAMIDE.

● Bases with two positive charges, *e.g.*



Δ Bases with no charge, *e.g.* aniline.

○ Bases with one negative charge, *e.g.* acetate ion.

▽ Bases with two negative charges, *e.g.* oxalate ion.

expression for the acid strength of the ion  $\text{OH}_3^+$  is (*cf.* equation (16) for the ammonium ion)

$$K_A(\text{OH}_3) = \frac{[\text{OH}_3^+][\text{H}_2\text{O}]}{[\text{OH}_3^+]} = 55.5 \quad (23)$$

The basic strengths of  $\text{OH}^-$  and  $\text{H}_2\text{O}$  are then conveniently measured by the reciprocals of these acid constants for their corresponding acids  $\text{H}_2\text{O}$  and  $\text{OH}_3^+$ . These values cannot be strictly compared with the corresponding ones for other acids and bases, since they involve the supposed volume concentration of  $\text{H}_2\text{O}$  molecules in water, a quantity which is clearly unsuited for use in the calculation of a mass action

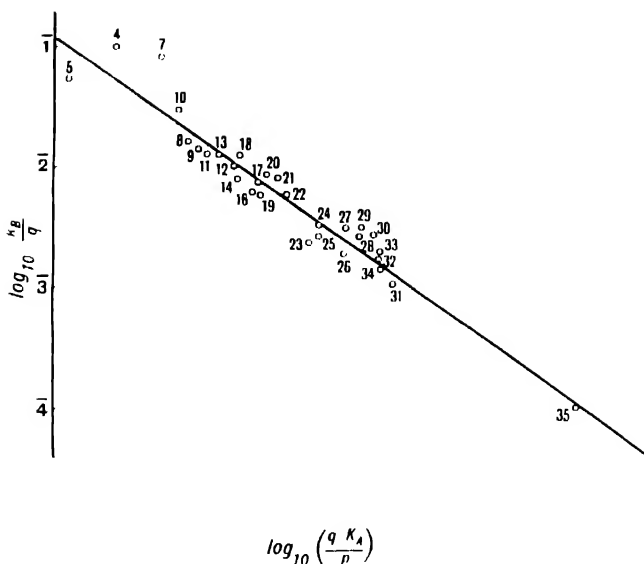


FIG. 3.—THE MUTAROTATION OF GLUCOSE.

Key to figures: 4 histidine, 5 *α*-picoline, 7 pyridine, 8 trimethylacetate ion, 9 propionate ion, 10 quinoline, 11 acetate ion, 12 phenylacetate ion, 13 glutamate ion, 14 benzoate ion, 16 *o*-toluate ion, 17 glycollate ion, 18 aspartate ion, 19 hippurate ion, 20 formate ion, 21 *α*-alanine, 22 mandelate ion, 23 salicylate ion, 24 *o*-chlorobenzoate ion, 25 chloroacetate ion, 26 cyanoacetate ion, 27 *p*-benzobutaine, 28 sarcosine, 29 lysine hydrochloride, 30 arginine hydrochloride, 31 sulphate ion, 32 proline, 33 dimethylglycine, 34 betaine, 35 water

constant: however, the values may serve to give a rough estimate of the acid-base strengths concerned. Moreover, in the case of catalysis by the water molecule the catalytic constant for  $H_2O$  has to be evaluated by dividing the "spontaneous" velocity  $k_0$  by the concentration of water molecules (55.5), so that the latter figure enters into the calculation of both the catalytic constant and the acid-base strength, and the

uncertainty attached to its use may to some extent cancel out in the comparison.

Some of the experimental data for catalysis by hydroxyl ions and water molecules are shown in Table XI. The water molecule is throughout acting as a base, and the calculated values of  $k_{OH^-}$  and  $k_{H_2O}$  are obtained from equation (21), using values of  $G'_B$  and  $\beta$  derived from the experimental data for other basic catalysts.

TABLE XI.—CATALYSIS BY HYDROXYL IONS AND WATER MOLECULES.

Reaction.	$k_{H_2O}$		$k_{OH^-}$	
	Obs.	Calc.	Obs.	Calc.
Decomposition of nitramide <sup>1</sup>	$6.8 \times 10^{-6}$	$8.2 \times 10^{-6}$	$1.0 \times 10^6$	$1.0 \times 10^9$
Mutarotation of glucose <sup>2</sup>	$9.6 \times 10^{-5}$	$6.6 \times 10^{-5}$	$3.8 \times 10^3$	$7.4 \times 10^2$
Iodination of acetone <sup>3</sup>	$5.0 \times 10^{-10}$	$8.0 \times 10^{-11}$	$1.5 \times 10$	$5.2 \times 10^4$
Iodination of acetylacetone <sup>3</sup>	$2.5 \times 10^{-9}$	$1.5 \times 10^{-10}$	$1.0 \times 10^2$	$5.5 \times 10^5$
Iodination of monochloroacetone <sup>3</sup>	$5.8 \times 10^{-8}$	$2.6 \times 10^{-8}$	$5.6 \times 10^2$	$1.5 \times 10^6$
Iodination of monobromoacetone <sup>3</sup>	$2.9 \times 10^{-7}$	$4.4 \times 10^{-8}$	$1.2 \times 10^4$	$1.0 \times 10^7$
Bromination of dichloroacetone <sup>3</sup>	$7.9 \times 10^{-7}$	$3.0 \times 10^{-7}$	$2.7 \times 10^4$	$1.4 \times 10^7$
Bromination of acetoacetic ester <sup>3</sup>	$1.3 \times 10^{-3}$	$4.3 \times 10^{-3}$	—	—
Bromination of acetylacetone <sup>3</sup>	$1.2 \times 10^{-2}$	$6.9 \times 10^{-2}$	—	—
Bromination of acetoacetic acid <sup>3</sup>	$1.4 \times 10^{-1}$	$6.5 \times 10^{-1}$	—	—

<sup>1</sup> Marlies and La Mer, J. Amer. Chem. Soc. 1935, **57**, 1812.

<sup>2</sup> Lowry and Wilson, Trans. Faraday Soc. 1928, **42**, 683.

<sup>3</sup> Bell and Lidwell, Proc. Roy. Soc. 1940, **A**, 176, 88.

This calculation normally involves an extrapolation through at least four powers of ten, and hence no weight can be attached to the presence or absence of exact agreement between observed and calculated values. In fact, the agreement to within a power of ten found for water catalysis is probably as good as can be expected, and confirms the view that the "spontaneous" reaction is in fact due to basic catalysis by water molecules. On the other hand, there is in all cases (except in the mutarotation of glucose) a large systematic discrepancy for catalysis by the hydroxyl ion, and it is likely that this represents a real effect, *i.e.* that the Brönsted relation is not applicable over the very wide range of basic strengths involved (*cf.* Bell and Lidwell, *l.c.*).

The application of the Brönsted relation to catalysis in *non-aqueous solutions* has been tested for a number of reactions and solvents. In many cases there are no data available for the acid-base strengths of the catalysts in the solvents in question, and in such cases the strengths in water have been commonly used for comparison. This procedure is justifiable, since there is much evidence to show that the relative strength of two acids of the same charge type is little affected by change of solvent: hence the use of strengths appropriate to another solvent will only have the effect of changing the value of the constant  $G$  in equations (19)–(21).

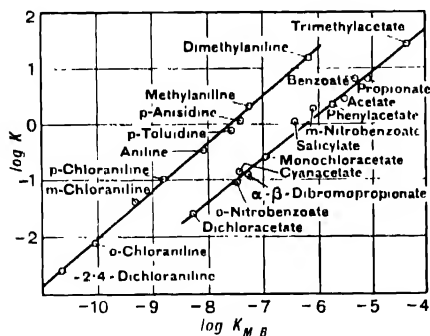


FIG. 4.—THE DECOMPOSITION OF NITRAMIDE IN *m*-CRESOL.

Figs. 4 and 5 illustrate the usual logarithmic plot for two catalysed reactions in non-aqueous solvents. In the decomposition of nitramide in *m*-cresol (Bronsted, Nicholson and Delbanco, *Z. physikal. Chem.* 1934, **169**, 379) the basic constants ( $K_{M,B}$ ) were obtained directly from indicator measurements in the same solvent. On the other hand, in the rearrangement of *N*-bromoacetanilide (to give *p*-bromoacetanilide) (Bell, *Proc. Roy. Soc.* 1934, **A**, **143**, 377) the acid constants given ( $K_0$ ) are those in aqueous solution.

#### (h) THE MECHANISM OF ACID-BASE CATALYSIS.

The term "catalysis" is often used to describe the promotion of a chemical change by some physical agency, as, for example, the effect of a

surface in a heterogeneous gas reaction, or of paramagnetic molecules in the conversion of para- to ortho-hydrogen. It was originally thought that catalysis by acids and bases was due to some physical effect of this kind, which was vaguely connected with the supposed small size of the hydrogen ion or the high mobilities of hydrogen and hydroxyl ions. However, modern views accept a much more "chemical" explanation, according to which catalysis by acids and bases is due to an *acid-base reaction between the catalyst and the substrate*. This view leads to the same kinetic laws as the physical picture of catalysis, provided that the extent of the reaction between the catalyst and the substrate is small, and that the catalyst emerges unchanged from that reaction. The catalyst is thus supposed to take an essential part in the reaction mechanism, and not merely to speed up an uncatalysed process. In confirmation of

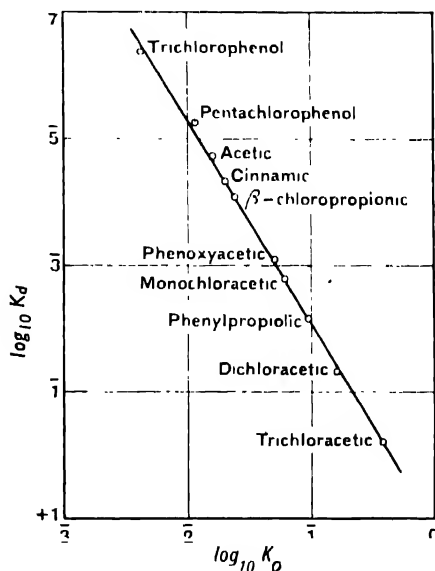


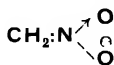
FIG. 5.—THE REARRANGEMENT OF *N*-BROMOACETANILIDE IN CHLOROBENZENE.

this view, it is generally found that reactions catalysed by acids and bases do not take place at all in the absence of catalysts (including catalytic impurities fortuitously present). As already indicated, the so-called "spontaneous" reaction in aqueous and similar solutions is not a truly spontaneous reaction, but depends upon acid-base catalysis by the solvent molecules. Further, the assumption of an acid-base reaction between catalyst and substrate provides a reasonable explanation of the existence of general catalysis by acids and bases, and of relations between catalytic power and acid-base strength.

Substances commonly acting as substrates are such weak acids or bases that their acidic or basic properties are barely detectable, and a simple acid-base reaction between catalyst and

substrate will normally proceed to such a small extent that no observable result is produced. In an actual catalysed reaction the products of this initial acid-base reaction must be capable of undergoing some further change leading to an observable result. For example, in the decomposition of nitramide it is suggested that the basic catalyst acts by removing a proton from  $\text{NH:NOOH}$ , the tautomeric form of nitramide, forming the ion  $[\text{N}:\text{NOOH}]^-$ , which is unstable and decomposes rapidly. In other cases it may be necessary to add another reagent to produce the reaction: e.g. in the reaction of acetone with halogens (basic catalysis) it is believed that the effect of the basic catalyst is to produce very small quantities of the ion  $[\text{CH}_2\text{CO}\cdot\text{CH}_3]^-$ , which then reacts rapidly with the halogen.

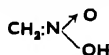
Acid base reactions (e.g. the neutralisation of acids and bases) usually take place at a rate too great for measurement, but it is believed that this is not always the case for the reactions between catalyst and substrate. Such slowness of reaction is associated with *mesomerism*, i.e. the existence of two possible electronic structures for the ion produced. This kind of behaviour is met with in an extreme form in substances known as pseudo-acids and pseudo-bases. For example, the normal form of nitromethane has the structure  $\text{CH}_3\cdot\text{NO}_2$ , and would not be expected to ionise to any appreciable extent in the presence of sodium hydroxide. Actually it reacts completely with sodium hydroxide to give a salt, though the reaction takes place at a measurable speed. This is because the ion formed is not  $\overset{\ominus}{\text{C}}\text{H}_2\text{NO}_2$ , but has the alternative electronic structure



The reaction with hydroxyl ions would not normally be classed as an example of catalysis, but the bromination of nitromethane is catalysed by bases like the acetate ion, and no doubt involves the formation of the same nitromethyl ion.<sup>1</sup>

In many cases, however (particularly in acid catalysis), the reaction between catalyst and substrate is assumed to be a rapid one, and the products of this reaction then undergo further but slow transformation. It is often difficult to determine the relative rates of the successive stages, and the matter is often complicated by the fact that acids and bases may take part in several stages of the observed change (e.g. Pedersen, J. Physical Chem. 1934, **38**, 581; Trans. Faraday Soc. 1938, **34**, 237; Bell, Proc. Roy. Soc. 1936, A, **154**, 414; "Acid-Base Catalysis," Oxford, 1941, Chapter VI; Skrabal, Z. Elektrochem. 1927, **33**, 322).

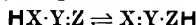
<sup>1</sup> It was formerly assumed that both the neutralisation and the bromination of nitro-paraffins involved the intermediate formation of the *aci*-form, e.g.



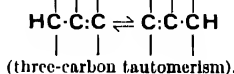
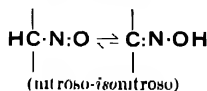
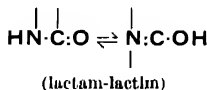
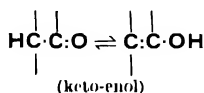
However, it has been shown clearly (Pedersen, Kgl. Danske Vid. Selsk. Math.-fys. Medd. 1932, **12**, No. 1; J. Physical Chem. 1934, **38**, 581) that the evidence is against the formation of undissociated *aci*-nitromethane in these reactions.

A very large amount of work has been done during the last twenty years on the mechanism of individual catalysed reactions (cf. Watson, "Modern Theories of Organic Chemistry," 2nd ed., Oxford, 1941; Hammett, "Physical Organic Chemistry," New York, 1940). The following examples are given of the kind of conclusions reached in two important groups of reactions—the prototropy of ketones, and the hydrolysis of esters—without going into the evidence on which these conclusions are based.

(i) **The Prototropy of Ketones.**—A large group of tautomeric changes are commonly described as *prototropic changes* and can be represented by the general scheme

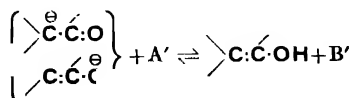
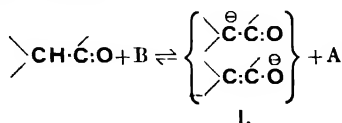


where X, Y and Z are normally either carbon, nitrogen or oxygen. The following are examples:

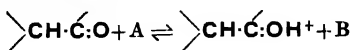


All these reactions are catalysed by acids and/or bases, and the accepted mechanisms involve the addition of a proton at one point of the molecule and the removal of a proton from another point; hence the term *prototropic*. In the interconversion of a keto form and an enol form (i.e. of ketones or related compounds) the supposed mechanisms are as follows, A representing an acid and B the corresponding base.

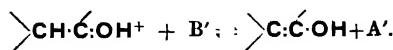
#### Basic Catalysis.



#### Acid Catalysis,



#### II.



It will be seen that in basic catalysis the second stage of the reaction involves reaction with an acid, while the second stage of acid catalysis involves reaction with a base. Normally it is not necessary deliberately to add both an acid and a basic catalyst. In a hydroxylic solvent the solvent molecules can act either as acids or bases as required, while in a solvent not possessing acid-base properties the acid or base required in the second stage can be identical with the product of the first stage: i.e.  $A' = A$  and  $B' = B$  in the above schemes.

The ion (I) formed in basic catalysis has been written with two different structures, differing only in their electronic distribution. In older views of the process it was supposed that the upper of these two structures was first formed from the ketone, and that it then changed rapidly into the lower structure. According to modern views these two forms have no separate existence, the actual state of the ion being a *resonance hybrid* (or mesomeric state) of the two classical structures represented by the formulae given. The excess negative charge is distributed between the carbon and oxygen atoms, and when the ion takes up a proton it may produce either the keto or the enol form.

The actual interconversion of keto and enol forms has only been studied in a very few cases, and cannot be observed in the case of simple ketones on account of the instability of the enol form. There are, however, a number of observable processes which are closely related to the reaction schemes given above. The ion (I) formed in basic catalysis reacts very rapidly with halogens, and many measurements have been made on the *halogenation of ketones* and related substances. The rate of reaction is independent of the nature and concentration of the halogen, being determined by the rate at which the ion (I) is formed by the reaction between the ketone and the catalyst. The rate of *isotopic exchange* between the ketone and a hydroxylic solvent containing deuterium is also determined by the rate of formation of the ion (I), and has been measured in a few instances. Finally, in an optically active ketone of the structure  $R_1R_2CH \cdot CO \cdot R$ , the *rate of racemisation* under conditions of basic catalysis will also be equal to the rate of formation of the ion (I), which is equally likely to revert to either optical antipode.

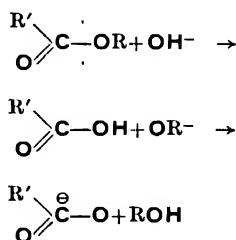
The halogenation and racemisation of ketones was originally believed to involve the actual production of the enol form, which is known to react rapidly with halogens and which cannot retain optical activity. However, it is now believed that under conditions of basic catalysis the formation of the ion is sufficient for both halogenation and racemisation, the enol not being produced. In acid catalysis, on the other hand, formation of the ion (II) will not lead to either racemisation, isotope exchange or reaction with halogen, and under these conditions actual formation of the enol is necessary for any of these processes to take place.

The above interpretation can be tested by comparing the rates at which the different processes take place under identical catalytic conditions. Under conditions of basic catalysis

it has been shown in one instance that the rates of racemisation and bromination are identical (Hsu and Wilson, J.C.S. 1936, 623), and in another instance that the rates of racemisation and deuterium exchange are identical (Hsu, Ingold and Wilson, *ibid.* 1938, 78). Similarly, for acid catalysis the equality of the rates of bromination and racemisation has been established for two ketones (Ingold and Wilson, *ibid.* 1934, 773; Bartlett and Stauffer, J. Amer. Chem. Soc. 1935, 57, 2580) and equality in the rates of bromination and deuterium exchange for another ketone (Reitz, Z. physikal. Chem. 1937, 179, 119): this would be expected if the equilibrium amount of enol is so small that the back reaction can be neglected.

(ii) The Hydrolysis of Esters.—The mechanism of this important class of reactions has been formulated in a large number of different ways. However, many of these differ only in a formal way, or in some details which cannot be tested experimentally. The schemes given here represent one of the simplest possible formulations (*cf.* Day and Ingold, Trans. Faraday Soc. 1941, 37, 686).

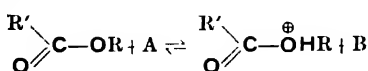
The hydrolysis of an ester by means of hydroxyl ions probably represents a specific reaction which is not properly classed as basic catalysis. It has been maintained (*e.g.* Dawson and Lowson, J.C.S. 1927, 2444) that other basic species such as the acetate ion can exert a catalytic effect, but the evidence for this is at best inconclusive. The probable mechanism for the reaction with hydroxyl ions can be written



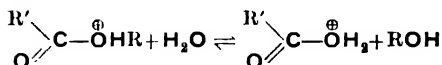
The first step of the reaction is in principle reversible, but since the second step goes to completion this reversibility is never observed. It will be seen that the bond between carbon and oxygen is broken (acyl fission), a supposition which is supported by experiments on oxygen isotope interchange and also by the retention of optical activity during hydrolysis when the group R is asymmetric.

The acid hydrolysis of an ester, on the other hand, represents a true case of acid catalysis. Attempts to establish catalysis by species other than hydrogen ions in aqueous solution (Dawson and Lowson, *ibid.* 1929, 393) are difficult to interpret with certainty owing to the high salt concentrations used. However, there is good evidence that the reverse reaction (esterification) is catalysed by undissociated acid molecules in alcohol solution (Rolfe and Hinshelwood, Trans. Faraday Soc. 1934, 30, 935; Hinshelwood and Legard, J.C.S. 1935, 587), and any proposed mechanism must therefore be consonant with

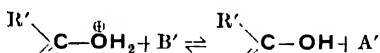
general acid catalysis. The first step can be written



where A is an acid (which may be the hydrogen ion) and B its corresponding base. The further reaction of the ion formed takes place according to the scheme



Thus change need not take place as a simple bimolecular reaction, but may involve preliminary fission of the ion. There are various possibilities for this detailed mechanism, which can in some cases be distinguished by the kinetic behaviour of the reaction, or by the optical behaviour (racemisation, retention of configuration or inversion) when R is asymmetric. The extent to which the different possibilities have been realised in practice is discussed in detail by Day and Ingold (*l.c.*). Finally the ordinary acid molecule is formed by the reaction:

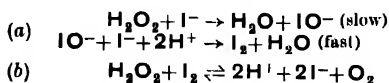


where the acid-base pair A'-B' may or may not be the same as that involved in the first step of the reaction. All the stages given are reversible, and the mechanism therefore applies both to hydrolysis and to esterification in the presence of acid catalysts.

#### (4) OTHER TYPES OF POSITIVE CATALYSIS IN SOLUTION.

There are a number of instances of homogeneous catalysis in solution which do not fall under the head of acid-base catalysis. In some of these enough is known about the mechanism to show that it depends on *alternate oxidation and reduction of the catalyst*, while in other cases the existence of several valency states makes it probable that the same type of explanation holds. The following examples illustrate the kind of behaviour met with.

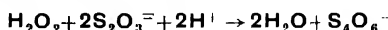
**The Decomposition of Hydrogen Peroxide** is catalysed by iodide ions in neutral solution, the reaction velocity being directly proportional to the concentrations of hydrogen peroxide and of iodide ion. The reaction mechanism has been elucidated by a number of workers (*see* summary by Bray, *Chem. Reviews*, 1932, 10, 172; *cf. also* Liebhafsky and Mohammed, *J. Amer. Chem. Soc.* 1933, 55, 3977). The following reactions can take place:



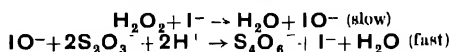
In a solution containing originally only iodide ions, reactions (a) only can take place to begin with. However, as soon as some iodine has been produced reaction (b) sets in, and after

a very short time the velocities of the two reactions become equal, the net result being  $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ . Since the reaction (b) has a much greater velocity constant than (a), the equilibrium amount of  $\text{I}_2$  is much smaller than that of  $\text{I}^-$ . The reaction velocity is therefore given by  $v = k[\text{H}_2\text{O}_2][\text{I}^-]$ , where  $\text{I}^-$  is practically equal to the original concentration of iodide ion. The velocity of reaction (a) can be measured separately by using solutions buffered to a moderate hydrogen ion concentration sufficient to prevent (b), and the velocity of iodine production is found to equal the rate of decomposition of hydrogen peroxide in neutral solution.

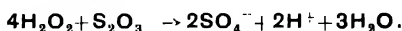
**The Reaction of Hydrogen Peroxide with Thiosulphates** is also catalysed by iodide ions. In this case there is an uncatalysed reaction represented by



the velocity of which is proportional to  $[\text{H}_2\text{O}_2][\text{S}_2\text{O}_3^{2-}]$ , and independent of  $[\text{H}^+]$ . The addition of iodide ions causes an increase in velocity which is proportional to  $[\text{H}_2\text{O}_2][\text{I}^-]$ , and independent of both  $[\text{S}_2\text{O}_3^{2-}]$  and  $[\text{H}^+]$ . This is explained (Abel, *Z. Elektrochem.* 1907, 13, 555) by the reaction scheme:



The same reaction is catalysed by molybdic acid, but in this case the products are different, the change being



The total rate of sulphate production (which must be disentangled from the tetrathionate production mentioned above) is given by an equation of the form

$$v = (k_1 + k_2[\text{H}^+])[\text{MoO}_3][\text{S}_2\text{O}_3^{2-}]$$

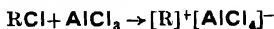
being independent of the concentration of hydrogen peroxide. It is assumed that all the molybdate is converted immediately by the hydrogen peroxide into the permolybdate ion  $\text{MoO}_6^{3-}$ , a small proportion of which reacts with the hydrogen ion to give  $\text{HMoO}_6^{2-}$ . Both the ions  $\text{MoO}_6^{3-}$  and  $\text{HMoO}_6^{2-}$  oxidise the thiosulphate to sulphate at measurable but different rates, forming molybdate, which is immediately reconverted to permolybdate by the hydrogen peroxide (Abel, *ibid.* 1912, 18, 705; *Monatsh.* 1912, 34, 425, 821).

**Catalysis by Metallic Ions** is met with in many reactions, though the mechanism is usually a matter of speculation. Many of the reactions involve oxidation or reduction, and in such cases the catalysing ion is normally one which can exist in more than one valency state: for example, it is well known that the decomposition of a hypochlorite solution to give oxygen is catalysed by cobalt salts, and it is supposed that the cobalt is alternately oxidised to the cobaltic state and reduced to the cobaltous state. Other examples are the decomposition of hydrogen peroxide, catalysed by chromate ions (Spitalsky and Koboseff, *Z. physikal. Chem.* 1927, 127, 129); the oxidation of iodides by hydrogen

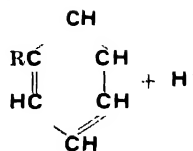
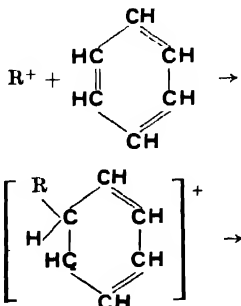


peroxide, catalysed by iron and copper ions, molybdates and tungstates (Brode, *ibid.* 1901, 37, 257); the oxidation of sulphites by oxygen, catalysed by iron and copper ions (Titoff, *ibid.* 1903, 45, 641); and the anodic oxidation of many substances, catalysed by ceric ions. A special type of behaviour is met with in some reactions of this kind, in that when two catalysts are present simultaneously, their effect is greater than the sum of their catalytic effects when present singly. This behaviour is often referred to as *promoter action*. Examples are the effect of copper and iron salts in the reaction between persulphates and iodides (Price, *ibid.* 1898, 27, 474), in the reaction between hydrogen peroxide and iodides (Brode, *ibid.* 1901, 37, 257), and in the reaction between sulphites and persulphates (Schilow and Buligin, Chem.-Ztg. 1913, 37, 512); also the effect of copper and mercuric salts in the oxidation of various organic compounds by concentrated sulphuric acid (Bredig and Brown, Z. physikal. Chem. 1903, 48, 502). It is possible to obtain a general explanation of this promoter action in terms of intermediate compounds even without a knowledge of the actual intermediate stages in any particular case (Spitalsky, *ibid.* 1926, 122, 257).

**Catalysis of Organic Reactions by Metallic Halogenides** (notably of aluminium, iron and boron) constitutes a different class of homogeneous catalysis. There is of course a large mass of literature on preparative organic chemistry which deals with this type of reaction, but only a few examples of recent work will be referred to in which evidence has been obtained of the mechanism of catalysis. The best known example is the *Friedel-Crafts reaction*, in which a hydrocarbon (usually aromatic) is alkylated or acylated by alkyl- or acyl-halogenides in the presence of *aluminium chloride* or other halogenides. It is now generally agreed (*cf.* Wertyporoch, Ber. 1931, 64 [B], 1375; Linstead, Chem. Soc. Annual Rep. 1937, 34, 251; Nightingale, Chem. Reviews, 1939, 25, 329) that the first step consists of the addition of the aluminium chloride to the organic halogenides to give a complex which is readily ionised, *e.g.*



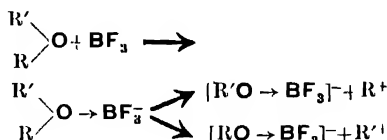
Recent evidence of this has been provided by exchange experiments using radioactive chlorine (Fairbrother, J.C.S. 1937, 503). The positive ion  $R^+$  or  $RCO^+$  then acts as the alkylating or acylating agent, *e.g.* with benzene :



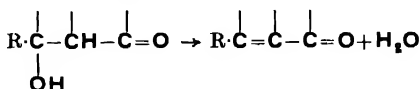
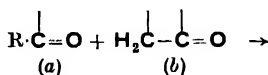
the aluminium chloride being regenerated by the reaction :



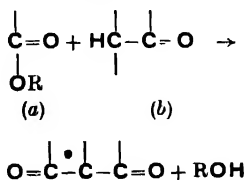
Of recent years *boron trifluoride* has been increasingly used in conjunction with alcohols, ethers and esters as an alkylating agent for hydrocarbons. The mechanism assumed is similar, *i.e.* (Price and Giskowski, J. Amer. Chem. Soc. 1938, 60, 2499)



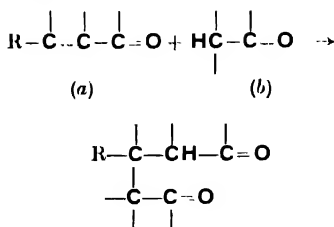
where R is an alkyl group, R' either alkyl, acyl or hydrogen, and the choice between the alternatives in the last stage depends on the nature of the groups. The positive ion then reacts with the hydrocarbon as above. As in all mechanisms of this kind, it may be left an open question whether the ion  $R^+$  exists in the free state, or whether the complex undergoes ionisation in this sense on the approach of the hydrocarbon. There is, however, a good deal of independent evidence of ionisation when  $BF_3$  interacts with organic oxygen compounds (Meerwein and Pannwitz, J. pr. Chem. 1934, [ii], 141, 123). Boron trifluoride has also been found to catalyse another class of reactions, which are usually effected by means of basic catalysts, though acid catalysts have also been used (Hauser and Breslow, J. Amer. Chem. Soc. 1940, 62, 2385). Among these are the aldol condensation, sometimes followed by loss of water, *i.e.*



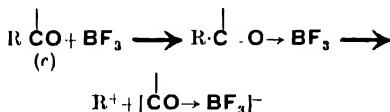
the Claisen condensation,



and the Michael condensation,

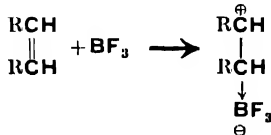


In the basic catalysis of these reactions it is supposed that the component marked (b) loses a proton to the basic catalyst, leaving behind a negatively charged carbonium ion which then reacts further, just as in the base-catalysed prototropy of ketones (*see* p. 256c). In catalysis by  $\text{BF}_3$ , on the other hand, the catalyst is supposed to add on to the component marked (c), *i.e.*



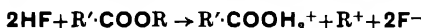
subsequent reaction being due to the ion  $\text{R}^+$ .

In addition to this wide range of reactions, it has been found that *cis-trans* isomerisation is also catalysed by  $\text{BF}_3$  (Price and Meister, *J. Amer. Chem. Soc.* 1939, **61**, 1595). The proposed mechanism is



followed by rotation about the single bond. The same equation is supposed to represent the first stage in the alkylation of benzene by olefins in presence of boron trifluoride.

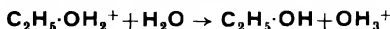
As already mentioned at the end of section (d), boron trifluoride ranks as an acid if we accept the definition of an acid as an electron-acceptor, although it is not termed an acid if (as is usual) this term is restricted to proton-donors. It is therefore of interest that *liquid hydrogen fluoride* (an acid according to either definition) has been found to act as a catalyst in many of the above reactions and rearrangements (*cf.* Simons, Archer and Randall, *ibid.* 1939, **61**, 1821; 1940, **62**, 485). It is known that practically all organic compounds containing oxygen dissolve in liquid hydrogen fluoride with the production of ions (Fredenhagen, *Z. anorg. Chem.* 1939, **242**, 23), and the mechanism of catalysis may be assumed to take place along similar lines. For example, when benzene is alkylated by an ester in liquid hydrogen fluoride, the first stage is



and the ion  $\text{R}^+$  then acts as an alkylating agent as before.

#### (k) NEGATIVE CATALYSIS IN SOLUTION.

Cases of negative catalysis (or inhibition) in solution are comparatively rare. It is fairly often found that the addition of small quantities of a substance may cause a considerable diminution in the velocity of a reaction, but in most cases this is due to *removal of a positive catalyst* by a chemical reaction. For example, in the esterification of carboxylic acids in alcohol solutions the addition of small quantities of water decreases the velocity, owing to the reaction:

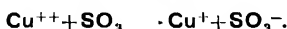


The effective catalyst is the solvated hydrogen ion  $\text{C}_2\text{H}_5\cdot\text{OH}_2^+$ , in comparison with which the hydrated ion  $\text{OH}_3^+$  has a very small effect (Goldschmidt and U'dby, *Z. physikal. Chem.* 1907, **60**, 728; 1910, **70**, 627). The effect of the inhibitor thus depends on the relation between its concentration and the concentration of positive catalyst, and the phenomenon would not usually be described as genuine negative catalysis. In some cases the concentration of the positive catalyst may be extremely small and its presence may be fortuitous. For example, the mutarotation of tetramethylglucose is difficult to arrest in most solvents, but does not take place in chloroform solution. This is attributed to the presence of traces of phosgene as an impurity, which reacts with and removes traces of catalysing amines, also present as impurities (Lowry *et al.*, *J.C.S.* 1925, **127**, 1385, 2883). Similarly, the inhibiting effect of gelatin on the decomposition of chloramine has been attributed to the formation of a complex with minute amounts of copper ions, which exert a positive catalytic effect (Bodenstein, *Z. physikal. Chem.* 1928, **A**, 139, 397).

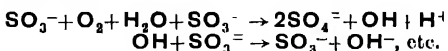
A different type of negative catalysis is met with in a number of oxidation reactions, notably the *oxidation of sulphites to sulphates* by oxygen gas. This reaction has been studied by many workers over a long period, but most of the modern work is due to Bäckström and his collaborators (Bäckström, *J. Amer. Chem. Soc.* 1927, **49**, 1460; Bäckström and Alyea, *ibid.* 1929, **51**, 90; Alyea, *ibid.* 1930, **52**, 2743; Alyea and Jeu, *ibid.* 1933, **55**, 575; Bäckström, *Z. physikal. Chem.* 1934, **B**, 25, 122). The rate is independent of the oxygen concentration, but depends on the hydrogen ion concentration and is increased by very small concentrations of various metallic ions, notably  $\text{Cu}^{++}$ . The rate is also greatly increased by illumination by ultra-violet light, the quantum efficiency of the photochemical reaction being in the neighbourhood of 50,000. Both the thermal and photochemical reactions are greatly inhibited by the addition of small concentrations of various organic compounds (notably alcohols), and this is true both in the presence and absence of cupric ions. It is now agreed that the oxidation consists of a *chain reaction*, and that the action of the inhibitor depends upon the breaking of the chains and the consequent shortening of their length. Since the chains in the uninhibited reaction involve the oxidation of many thousands of sulphite ions (as shown by the high quantum efficiency) the destruction of a very

small number of intermediates in these chains can produce a large decrease in reaction velocity. It is assumed that the act of chain breaking involves the oxidation of the alcohol (or other inhibitor), and it has proved possible to detect the very small amounts of oxidation products formed, and to show that the rate at which they are produced agrees with the shortening in the chain length of the sulphite oxidation.

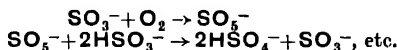
There is still some difference of opinion as to the actual nature of the reaction chain. Most workers agree that the primary process is the production of the singly charged ion  $\text{SO}_3^-$  by loss of an electron from  $\text{SO}_3$ , as suggested by Haber (Naturwiss. 1931, 19, 450; Haber and Franck, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1931, 250). The positive catalytic effect of cupric ions is then explained by the reaction



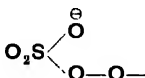
According to Haber the subsequent chain process is



where the chain can be broken by the oxidation of the inhibitor by the radical  $\text{OH}$ . Other writers prefer a mechanism involving hydrogen peroxide in place of the radical  $\text{OH}$ , while Backstrom (Z. physikal. Chem. 1934, B, 25, 122) writes



the chain breaking being caused by oxidation of the inhibitor by the ion  $\text{SO}_5^-$ , considered to have the structure



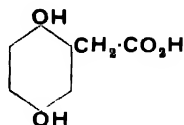
Similar behaviour is met with in the oxidation of aldehydes in solution by gaseous oxygen, this reaction also being a chain reaction promoted by metallic ions and by ultra-violet light, and inhibited by alcohols (*cf.* Backström, *l.c.*). In this case, however, the position is more complicated, since the amounts of inhibitor oxidised do not agree with those calculated on the basis of a simple chain-breaking mechanism. The literature contains many other examples of negative catalysis which have not been studied in detail, but which probably all depend on breaking of reaction chains. For example, the so-called "activated oxalic acid" (prepared by the action of potassium permanganate on an excess of oxalic acid) probably involves free radicals of long life, and its activity is greatly reduced by small concentrations of many oxidisable substances, notably phenols and certain dye-stuffs in concentrations as low as  $10^{-7}\text{N}$ . (Weber, *ibid.* 1934, B, 25, 363).

**Bibliography.**—E. K. Rideal and H. S. Taylor, "Catalysis in Theory and Practice," Macmillan, 1926; J. N. Brönsted, "Acid and Basic Catalysis," Chem. Reviews, 1928, 5, 231; G.-M.

Schwab, H. S. Taylor and R. Spence, "Catalysis," Macmillan, 1937; R. P. Bell, "Acid-Base Catalysis," Oxford, 1941.

R. P. B.

### HOMOGENISERS (v. Vol. IV, 295c). HOMOGENTISIC ACID,



I.

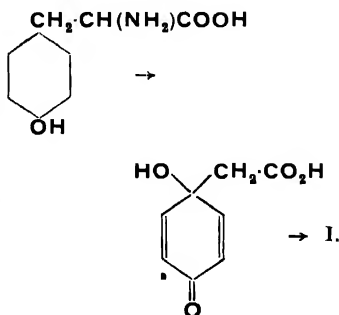
2:5-Dihydroxyphenylacetic acid, m.p. (anhydrous) 152–154°.

The acid occurs in the urine of individuals suffering from alkaptonuria, the urine becoming brown on the addition of alkali in the presence of oxygen. It also occurs in the blood of alkaptonurics. The acid was first isolated and identified by Wolkow and Baumann (Z. physiol. Chem. 1891, 15, 241).

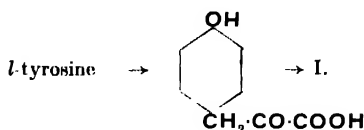
To 100 ml. of urine 5–6 g. lead acetate are added, boiled, and the  $p_H$  adjusted to 5–6 by the addition of aqueous ammonia, and the lead salt allowed to crystallise. After recrystallisation under similar conditions the salt is decomposed with hydrogen sulphide. Finally the solution is concentrated under reduced hydrogen pressure and saturated with sulphur dioxide, the acid separating on cooling (G. Medes, A. 1934, 206).

The homogentisic acid found in the urine probably arises from degradation of tyrosine and phenylalanine (O. Neubauer, Chem. Zentr. 1909, II, 50; L. Blum, Arch. exp. Path. Pharm. 1908, 59, 273). Whether its presence is due to the failure of the alkaptonuric to destroy the homogentisic acid when formed, or to abnormal katabolism is not known (O. Gross, Biochem. Z. 1914, 61, 165; A. J. Wakeman and H. D. Dakin, J. Biol. Chem. 1911, 9, 139; H. D. Dakin, *ibid.* 1911, 9, 151).

According to Blum (*l.c.*) and E. Friedmann (Beitr. chem. Physiol. Path. 1908, 11, 304), in the conversion of tyrosine into homogentisic acid the side chain is first degraded, then a relative change of position of the side chain and the hydroxyl group takes place, with a secondary oxidation concurrently; finally a reduction occurs,

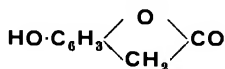


According to Y. Kotake (Chem. Zentr. 1923, I, 117) the change occurs as follows:



Homogentisic acid may be synthesised by heating quinol dimethyl ether dissolved in carbon disulphide with ethyl chloroacetate and aluminium chloride and subsequent demethylation with fuming hydriodic acid and red phosphorus (Osborne, J. Physiol. 1903, 29, 14; Baumann and Frankel, Z. physiol. Chem. 1895, 20, 224). Also from the allyl ether of quinol monobenzoate (G. Hahn and W. Stenner, *ibid.* 1929, 181, 88).

Homogentisic acid passes into the lactone,



m.p. 191°, on heating. The lead salt has m.p. 214–215°, it is soluble in 675 parts of water at 20°. *Ethyl ester*, m.p. 119–120°.

Homogentisic acid readily reduces copper and silver salts; it gives a blue colour with ferric chloride and on distillation from ferric chloride solution gives a substance, m.p. 89–90° (C. T. Morner, *ibid.* 1921, 117, 67). It yields *gentisic* acid (hydroquinone carboxylic acid) on fusion with potassium hydroxide at 196–198°. With amines it gives characteristic colours (C. T. Morner, *ibid.* 1910, 69, 329).

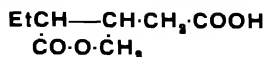
*Estimation*.—The acid may be estimated in milk and blood by precipitating the albumin with sodium tungstate and estimating the acid in the filtrate colorimetrically with phosphotungstic acid (H. Lieb and F. Lanyar, *ibid.* 1931, 203, 135; cf. H. P. Briggs, J. Biol. Chem. 1922, 51, 453, and G. Katsch and E. Metz, Chem. Zentr. 1928, I, 386).

In urine the homogentisic acid may be estimated iodometrically (H. Lieb and F. Lanyar, Z. physiol. Chem. 1929, 181, 199; E. Metz, Biochem. Z. 1927, 190, 261). The method depends on the oxidation of homogentisic acid to the quinone with 0.05*N*-iodine in bicarbonate or borax solution until a blue colour is obtained with starch. Providing no other interfering substances are present to react with the iodine, the method is quantitative. Addition of a large amount of sulphuric acid liberates the iodine which can be titrated with sodium thiosulphate, and where small amounts of homogentisic acid are present, addition of potassium iodide is advisable. The amount of thiosulphate in determining the amount of the acid in 10 ml. urine is about 0.2 ml. too small and this correction must be added to give the true value, maximal error 0.5 mg. in 10 ml. 0.05*N*-solutions are used: 1 ml. thiosulphate is equivalent to 0.0042016 g. homogentisic acid.

For further details on the identification and estimation of homogentisic acid, see Abdenhalden, "Handbuch der biologische Arbeitsmethoden," Abt. 4, Teil. 5, i, 551 (1931).

**HOMOPHLEINE** (v. Vol. IV, 336a).

**HOMOPILOPIC ACID.**  $\alpha$ -ethylbutyrolactone acetic acid (H. A. D. Jowett, J.C.S. 1901, 80, 1345),



Oxidation of *isopilocarpine* with permanganate gives homopilopic acid, and pilopic acid,  $\text{C}_7\text{H}_{10}\text{O}_4$ , and the former on fusion with potash yields  $\alpha$ -ethyltricarballic acid. The acid is an oil, b.p. 235–237°/20 mm. It has been synthesised by N. A. Preobrashenski, A. M. Poljakowa and W. A. Preobrashenski (Ber. 1935, 68 [B], 844), and by Dey (J.C.S. 1937, 1057). These authors obtained the racemic acid in the solid form, m.p. 100°C. N. A. Preobrashenski and his colleagues have also synthesised *d*-homopilopic acid (Ber. 1935, 68 [B], 850).

**HOMORENON** (v. Vol. I, 147d).

**HOMRA** (v. Vol. II, 145d).

**HONEWORT**, Corn Parsley (*Petroselinum segetum*), American names, *Cryptolania canadensis*, *Nison Amomum*, an umbelliferous plant used as a salad in China and Japan. The leaves are also cooked and eaten as a vegetable. Chung and Ripperton (Hawaii Agric. Exp. Sta. Bull. 1929, No. 60) report the composition of marketable leaves as: water, 89.53; protein, 2.33; fat, 0.23; N-free extract, 4.37; fibre, 1.45; ash, 2.09%. Among mineral constituents of the leaves, Ca 0.114, Fe 0.015 and P 0.06% are noteworthy.

(Cf. Murray's "New English Dictionary," and Britten and Holland, "Dictionary of English Plant Names," 1886. The plant was believed to cure a swelling, "hone," in the cheek.)

A. G. Po.

**HONEY.** The syrupy excretion of the working bee (*Apis mellifica*) derived from nectar collected from flowers. It is deposited in the honeycomb cells as a reserve food-stock for the colony when external supplies are no longer available. The yellow syrupy fluid consists of nearly equal proportions of glucose and fructose with water and small quantities of nitrogenous matter, pollen, wax, mineral matter and acids, and occasionally sucrose and mannitol. Traces of alcohol are generally present. Honey also contains invertase, and possibly other enzymes derived from pollen, and traces of vitamins.

The colour of honey varies considerably with the source of nectar, heather honey being a rich golden-yellow and clover honey a pale greenish-white. In stored honey the colour may change somewhat during processing or subsequent storage according to conditions adopted. The specific gravity of honey is largely controlled by climatic conditions, values quoted in the literature varying from 1.10 to 1.45. The  $p_H$  value ranges from 3.8 to 4.3. Honey is usually laevorotatory (–9.1 to –3.0°) although dextrorotary samples occur. Heather honey may exhibit the property of thixotropy. A physical examination of such a honey is recorded by G. W. S. Blair (J. Physical Chem. 1935, 39, 213).

Analyses of honeys show considerable differences according to their place of origin. Excluding obviously abnormal samples the following ranges of composition apply to honeys from all parts of the world :

Water . . . . .	8-25
Glucose . . . . .	30-42
Fructose . . . . .	23-39
Sucrose . . . . .	0-4
Ash . . . . .	0.2-2.5

The ratio fructose : glucose is regarded by some analysts as sufficiently characteristic to serve as an index of the purity of commercial honeys. Thus Auerbach and Bodlander (Z. Unters. Nahr.-u. Genussm. 1924, 47, 233) state that the ratio should be 106-119:100 for genuine honey and may be <90:100 in artificial honeys. This view is not generally upheld and analytical data from numerous sources throw doubt on the validity of this statement. In Italian honeys, for example, Canneri and Salani (Ann. Chim. Appl. 1935, 25, 397) find the ratio for a great many samples to be in the range 101-113:100 but also record others showing ratios up to 168:100.

The sucrose content of honey also shows considerable variation, and although less than 1% in most European honeys it may reach much higher values under certain conditions. A sample of Hungarian honey examined by Berkó and Kardos (Mezőg. Kutat. 1937, 10, 177), in a season when the nectar flow was exceptionally high, contained more than 10% of sucrose. Follett-Smith (Div. Repts. Dept. Agric. Brit. Guiana, 1934, 100) reports British Guiana honey containing 8.67% of sucrose, the total sugars being 75.8% and the  $p_H$  4.23. It is said that bees fed on large proportions of sucrose invert only a portion of it and an abnormally large amount remains in the honey. Honey collected in the neighbourhood of Cuban sugar factories is reported to contain *artificially* inverted sugar. Bees fed exclusively on glucose produce honey containing that sugar only. Certain varieties of Sumatra honey produced by *Apis indica* consist largely of glucose and fructose but contain neither sucrose nor dextrin. "Honey," without comb, made by an Ethiopian mosquito in tree hollows, is recorded by Villiers (Compt. rend. 1878, 88, 292) to contain : water, 25.5; glucose and fructose, 32.0; mannitol, 3.0; dextrin, 27.9; ash, 2.5%. The Mexican honey-ant produces "honey" consisting of an almost pure solution of fructose. The product from *Polybia apicipennis* frequently includes large crystals of sucrose. "Eucalyptus honey," made by an Australian black bee, is a thick syrup having a strong aromatic odour. "Palm honey," the concentrated sap of *Jubaea spectabilis*, is commonly utilised in Chile and differs from genuine honey in its high sucrose content. Schmidt-Hebbel and Toledo (Pharm. Zentralk. 1938, 79, 633) record numerous analyses of this product, the notable figures in their average values being, water, up to 38%, and ratio sucrose : glucose+fructose not less than 4 (the corresponding values for Chilean honey are 20% and 0.1 respectively). American honey-

dew honey occasionally contains melezitose in considerable amounts (Hudson and Sherwood, J. Amer. Chem. Soc. 1920, 42, 116). This polysaccharide is also reported in conifer honey by T. von Fellenberg (Mitt. Lebensm. Hyg. 1937, 28, 139) who describes methods for its determination.

Both conifer and honey-dew honey frequently contain dextrins (Hilger, Z. Nahr.-u. Genussm. 1904, 8, 110; Haenle and Scholz, *ibid.* 1903, 6, 1027). After removal of protein matter by tannic acid, dextrin is separated from honey by precipitation with ether from acidified alcohol; it is strongly dextrorotatory, and probably accounts for the supposedly abnormal dextrorotation of honey samples, long regarded as a definite indication of adulteration by commercial syrups.

Small amounts of organic acids are commonly found in honey. Formic acid is said to be added by the bees prior to capping the comb, and possibly explains the small tendency of honey to ferment. Recorded formic acid contents of honey range from 0.006 to 0.01%. Nelson and Mottern (Ind. Eng. Chem. 1931, 23, 335), in an examination of very acid honeys, found acetic acid (up to 0.04%), citric acid (0.008%), malic acid (0.05%) and small amounts of succinic acid.

Honey usually contains traces of nitrogenous matter which is partly precipitated on dilution with water. Hungarian honey is said to contain peptones, globulin and some albumin, but not protamines, histones or albumoses. A considerable proportion of the nitrogen compounds in honey exists in colloidal forms and, in the case of American honeys, these show an isoelectric point in the neighbourhood of  $p_H$  4.3 (Lothrop and Paine, Ind. Eng. Chem. 1931, 23, 328). The colloidal matter contains 8-11% of nitrogen and is closely related to the colour of the honey. Dark-coloured honey is of high colloid content and removal of the colloid by ultrafiltration or by clarification with bentonite improves the colour of the honey and in many cases its flavour and storage properties. Paine, Gertler and Lothrop record 0.08% of colloids in pale (clover) and 0.80% in dark buckwheat honey (Ind. Eng. Chem. 1934, 26, 73). The non-colloids include a proportion of amino-acids which react with glucose and fructose to produce dark melaninoid colouring matter (Watanabe, J. Biochem. Japan, 1932, 16, 163). The darkening of honey on heating or during storage is attributable to this reaction.

It is not clear whether these nitrogenous colloidal substances are essential constituents of honey itself or whether they are derived from pollen which is almost invariably present. According to Butcher (Food, 1935, 4, 169) water-insoluble matter in honey should consist only of pollen grains. These may be separated by flotation on a 30-50% solution of honey. Microscopical examination of the pollen is frequently of value in honey investigations. A detailed system of microscopical examination of honey is described by Zander (Angew. Chem. 1935, 48, 147).\*

Enzymes occurring in honey include invertase, catalase, amylase and diastase. Neither lactase,

proteases nor lipases have been detected. The invertase, which is destroyed by heating honey to 60°, effects the slow hydrolysis of sucrose during storage of honey (Kardos, Z. Unters. Lebensm. 1938, 76, 354). Diastase is probably derived from pollen, and the diastatic activity of honey is often regarded as an index of its genuineness. Diastase is destroyed by heating honey to 70° for 1 hour. After 24 hours at 60° however the enzyme is still active.

Cold-run or "virgin" honey is obtained by uncapping the comb with a warm knife and either allowing the syrup to flow out at ordinary temperature or, more rapidly, by means of a centrifugal "extractor." Extracted comb may be replaced in the hive for refilling by the bees, or warmed and pressed to remove residual honey. The product thus obtained is usually inferior in colour to cold-run honey. In the latter, inversion of sucrose takes place fairly rapidly during the first 10-12 days of storage and much more slowly afterwards. The changes are accelerated by high storage temperature, as also is the rate at which the colour deepens (Lynn, Englis and Milum, Food Res., 1936, 1, 255). The latter phenomenon is dependent on the decrease in stability of fructose with rise in temperature and the greater tendency to react with amino-acids to form coloured substances (V. G. Milum, Amer. Bee J. 1939, 79, 445). In general, high temperatures of processing merely facilitate changes which take place slowly at lower temperatures, and do not introduce new factors. Freshly-drawn honey can be stored in darkness without change for some considerable time, but exposure to light accelerates sugar crystallisation.

Fermentation of stored honey is uncommon, and is dependent on the water content and on storage temperature; it is unlikely to occur at temperatures below 11° or above 26°. Honey of high water, nitrogen, acid and ash contents are liable to ferment when stored at 11-18°. According to Lochhead (Prog. Rept. Dominion Agric. Bact. Canada, 1934, 12) honey containing less than 17% of water does not ferment even after storage for a year. With 20% moisture, however, fermentation may occur at any time. Addition of 0.25-0.50% of sodium benzoate effectively prevents fermentation for a considerable period. The alcoholic beverage, mead, has been made since very early days by the controlled fermentation of honey. A supplementary source of nitrogen for the yeast is now usually added (Osterwalder, B., 1932, 858). According to Boussingault (Ann. Chim. 1872, [iv], 26, 362) the amount of carbon dioxide and of alcohol produced during fermentation is greater than would be expected from the quantity of sugar destroyed. Neither acetic nor lactic acid is produced during fermentation and the diastatic activity of the honey remains unchanged.

Honey is used medicinally as a mild laxative for children; it also acts as a demulcent, relieving dryness of the mouth and throat and facilitating swallowing. For these purposes honey is purified by warming and straining through warm flannel. The product is known as *Mel depuratum*.

Nottbohm (Arch. Bienenkunde, 1928, 8, 32) gives the following analysis of the ash of honey:

	(% of ash.)				
	K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	P <sub>2</sub> O <sub>5</sub> .
Blossom honey	30-50	5.5-10.0	2.1-8.0	1.5-2.1	1.6-12.5
Honey-dew honey	52-57	3.2-4.3	0.5-1.3	0.7-2.3	6.6-9.5

Paine, Gertler and Lothrop (*l.c.*) find that the separated colloids of honey include 2-9% of ash material. The ash of the colloids of sumac honey has the percentage composition:

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	P <sub>2</sub> O <sub>5</sub> .	K <sub>2</sub> O.	MgO.
42.6	22.6	14.3	9.0	9.6	trace

Spectroscopic examination of honey ash by Gorbach and Windhaber (Z. Unters. Lebensm. 1939, 77, 337) revealed the presence of Ca, Mg, Fe, Mn, P, Si, Cu and Ni in all honeys, but the spectrum region used, 210 m $\mu$  to 460 m $\mu$  is not suitable for detecting the alkali metals Li, Na, K. Forest honeys frequently contained Ba, Ag, Pd, V, U, Al, Ir, Co, Zn, As, Sn, Pt, Mo, and occasionally Ti, Cr, K and Sr. Admixture of 1% of forest honey with floral honey could be detected by this means.

The colour of natural honey appears to be related to the amount and composition of the ash as well as to its N and colloid contents and to its diastatic activity (*see above*). Whether these are related or independent phenomena is not clear. Schuette and Triller (Food Res. 1938, 3, 543) note a parallelism between colour and S and Cl contents and also between colour and Na and K contents (*ibid.* 1939, 4, 349). Lothrop and Paine (*l.c.*) also find that the percentage of nitrogen and the total ash in American honeys increases with depth of colour. Buttner (Z. Unters. Lebensm. 1935, 70, 475; 1938, 76, 351) records that the S content of floral honeys is extremely small, that of conifer honey somewhat greater (1.3-7.3 mg. [as SO<sub>4</sub>] per 100 g.) and that of synthetic honey may be as high as 36 mg. per 100 g.

The vitamin content (A, B, C and D) of honey is very small (Kifer and Munsell, J. Agric. Res. 1929, 39, 355). Griehel (Z. Unters. Lebensm. 1938, 75, 417) reports that honey mainly derived from *Mentha* species contained 1.6-2.8 and that mainly from buckwheat 0.07-0.22 mg. of vitamin-C per gram.

According to Dingemanse (Acta brev. neerl. Physiol. Pharmacol. Microbiol. 1938, 8, 55) certain honeys contain a volatile oestrogenic substance which may belong to the propylene-phenol group.

Much of the analyst's interest in honey centres round the distinction between genuine natural and adulterated or purely synthetic honeys, the position being complicated by the fact that hot-processed honey may have lost certain of the characteristics of natural honey (enzyme activity, etc.) and taken on certain of the attributes of adulterated honeys. The customary adulterants are commercial syrups, starch sugars, invert sugars, molasses, etc. Commercially inverted sugars normally contain

by-products (e.g. furfuraldehyde derivatives) which give colour reactions with  $\beta$ -naphthol or resorcinol. Fiehe's test (Z. Nahr.-u. Genussm. 1908, 16, 75; see also Fiehe and Stegmüller, Arb. Kais. Gesundh. 1912, 40, 305; J.S.C.I. 1912, 31, 943) is the most popular of this kind. This is carried out by treating the filtered and evaporated ether extract of honey with a solution of resorcinol (1%) in 25% hydrochloric acid. An orange-to-red colour indicates the presence of artificially inverted sugar. Genuine honeys normally give only a faint transient colour, even after processing at 60–65°. The reaction is more marked if the honey has been autoclaved 110–115° (Moreaux, Ann. Falsif, 1936, 29, 22). Exceptional cases have been recorded in which genuine honeys give a positive Fiehe test. Mathieu (*ibid.* 1938, 31, 97) considers that honey should not be regarded as adulterated unless it gives a more marked test than does genuine honey mixed with 2% of sucrose.

More recently the original Fiehe test has been largely replaced by the phloroglucinol test for hydroxymethylfurfuraldehyde. The technique is the same except that phloroglucinol replaces resorcinol in the acid reagent (Fiehe and Kordatzki, Z. Unters. Lebensm. 1929, 57, 468). The reagent gives no colour with pine honey, a temporary coloration with over-heated honey, and a deep red colour and red-brown precipitate with adulterated honey.

$\beta$ -Naphthol used similarly gives a red-to-violet coloration with honey containing commercial invert sugar (Litterscheid, J.S.C.I. 1913, 32, 376).

Hydroxymethylfurfuraldehyde may also be detected and estimated by Weiss' method (Z. Unters. Lebensm. 1929, 58, 320). An ethyl acetate extract of the honey is treated with *p*-nitrobenzhydrazide in acetic acid. Lemon yellow crystals of the hydrazone of the aldehyde are formed, m.p. 206–208° (decomp.), and may be dried and weighed. No precipitate is formed from genuine honey and that from heated honey is extremely small.

Dextrins present in starch syrups may be detected in adulterated honey by precipitation with methyl alcohol from a concentrated aqueous solution of honey. Alternatively, honey is dissolved in glacial acetic acid (4–5 g. of honey in 1 c.c. of acid) and dextrins if present in appreciable amounts separate from the solution (Raikov, Z. anal. Chem. 1939, 116, 40). Fiehe tests for dextrins in honey, after precipitation of protein matter with tannic acid, by addition of hydrochloric acid and alcohol. Pure honey remains clear under these conditions, whereas added starch syrup causes a turbidity.

According to Elsdon (Analyst, 1938, 63, 422) added glucose may be detected by the lowered freezing-point of a 10% solution of honey.

Adulteration of honey with molasses may be detected by Beckmann's test for raffinose. Sucrose is readily determined by means of the reducing power of honey before and after inversion. Although gross adulteration with sucrose may thus be shown, the sucrose content of genuine honey is itself variable over a considerable range and a limiting value indicative of adulteration is not easily decided. For similar reasons the

diastatic activity of honey, at one time taken as a criterion of purity, can no longer be regarded as trustworthy (Vansell and Freeborn, J. Econ. Entom. 1930, 23, 428; Lampitt, Hughes and Rooke, Analyst, 1930, 55, 666). Schou and Abildgaard (Dansk Tidsskr. Farm. 1931, 5, 89; Z. Unters. Lebensm. 1934, 68, 502) distinguish natural from artificial honey by differences in the ultra-violet absorption spectra. The curve for natural honeys rises smoothly from  $\lambda$ 380 to 220  $m\mu$  whereas that of adulterated samples shows a well-defined maximum at 282.5  $m\mu$  due to the presence of hydroxymethylfurfuraldehyde, of which invert sugar may contain up to 5%.

According to Gottfried (Z. Unters. Lebensm. 1929, 57, 558) the formal titration of genuine exceeds that of adulterated honey.

An ammoniacal solution of silver oxide (Ley's reagent) on warming with a concentrated solution of honey in water gives a greenish coloration; with adulterated samples the liquid becomes dark brown or black (Utz, Z. angew. Chem. 1907, 20, 993).

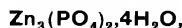
A. G. Po.  
**HONEYSUCKLE PERFUME.** There are a large number of species of *Lonicera* (Fam. Caprifoliaceæ), and in Provence the flowers of *L. caprifolium*, *L. etrusca* and *L. gigantea* are processed for the natural perfume of honeysuckle. Ingolen (Parfums France, 1937, 15, 299) obtained 3.3% of a green concrete extract from the flowers of *L. gigantea*, by extraction with light petroleum. From this 2.14% of essential oil was obtained, which had  $d^{20}_D$  0.9012; optically inactive;  $n^{20}_D$  1.4613°; ester value 145.6. The perfume as sold is practically entirely artificial, with a little natural ylang-ylang and neroli oil. Linalool, geraniol, hydroxycitronellal, phenylethyl alcohol and similar bodies are used in its preparation, but it does not in any way approach the perfume of the flower.

E. J. P.  
"HONTHIN." Trade name for keratinised tannin albuminate, used in treating intestinal catarrh (Von Sztankay, Pharm. Zentralk. 1932, 73, 630).

**HOOLAMITE** (v. Vol. III, 21a).

**HOPCALITE** (v. Vol. II, 347a; III, 19b, 20d, 21a).

**HOPEITE.** Hydrated zinc phosphate,



crystallised in the orthorhombic system. The crystals are remarkable in consisting of an intimate zonal intergrowth of two modifications —  $\alpha$ -hopeite and  $\beta$ -hopeite — differing in their optical characters and in the rate at which water is expelled by heat. They are colourless, white or brownish; sp.gr. 3.0–3.1; hardness 3½. For many years hopeite was known only as a rare mineral from the zinc mine of Altenberg, or Vieille Montagne, between Liège and Aachen; but in 1907 it was found finely crystallised and in considerable quantity in a cave with bone-breccia and associated with ores of zinc and lead at Broken Hill in Northern Rhodesia. In 1916 it was incorrectly described under the new name hibbenite from the Hudson Bay zinc mine near Salmo in British Columbia.

*Parahopeite*, from Broken Hill, Northern Rhodesia, has the same composition as hopeite, but the crystals are triclinic with sp.gr. 3-31 (L. J. Spencer, Min. Mag. 1908, 15, 18).

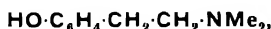
L. J. S.

### HOPKINSON PRESSURE BAR TEST

(v. Vol. IV, 549a).

HOPS (v. Vol. II, 91c.).

**HORDENINE** [*p*-( $\beta$ -dimethylaminoethyl) phenol],



was discovered by Léger (Compt. rend. 1906, 142, 108) in malt culms. No hordenine has been detected during the germination of wheat, peas or lupins (cf. Reihes, Amer. Chem. Abstr. 1936, 30, 7146) nor is it present in ungerminated barley (cf. Torquati, Chem. Zentr. 1911, 1, 166). During the process of germination the amount of hordenine is said to be increasing until the 11th day and then gradually diminishing (Raoul, Compt. rend. 1937, 205, 450; cf. Torquati, *l.c.*). For further constituents of the malt germs, see Hashitani (J. Tokyo Chem. Soc. 1919, 40, 647). Hordenine (*Anhaline*) occurs also in *Anhalonium* species (Spath, Monatsh. 1919, 40, 129; 1921, 42, 263). For extraction of hordenine from barley germs, see e.g. Gaebel (Arch. Pharm. 1906, 244, 436) or Raoul (Compt. rend. 1934, 199, 425) the yield is stated to be 0.13% of the air-dried malt germs. Hordenine forms colourless orthorhombic prisms, m.p. 117-118°, b.p. 173-174°/11 mm., subliming at 140-150°. The free base is readily soluble in EtOH,

soluble in  $\text{H}_2\text{O}$  (7 in 1,000 parts) and sparingly so in  $\text{C}_6\text{H}_6$ , toluene or xylene. It is a strong base, alkaline towards litmus and phenolphthalein, and liberates ammonia from its salts. It also reduces acid solutions of  $\text{KMnO}_4$  in the cold, and iodic acid and ammoniacal solutions of  $\text{AgNO}_3$  on warming.

The salts are crystalline: *hydrochloride*, m.p. 176.5-177.5°; *hydrobromide*, 173-174° *sulphate*, 209-211°, *methiodide*, 229-230° (179-180°, Hashitani, *l.c.*). *Benzoylhordenine*, m.p. 47-48° (see Léger, Compt. rend. 1907, 144, 208) For colour reactions of hordenine, see Denigès (Bull. Soc. chim. 1908, [iv], 3, 786) and Labat (J. Pharm. Chim. 1909, [vi], 29, 433).

By oxidation of *O*-methylhordenine with  $\text{KMnO}_4$  anisic acid was obtained (Gaebel, *l.c.* cf. Léger, Compt. rend. 1906, 143, 916) and a Hofmann degradation of the same substance afforded trimethylamine and vinylanisole (Léger, *ibid* 1907, 144, 488).

Hordenine was first synthesised by a series of reactions starting with phenylethyl alcohol (Barger, J.C.S. 1909, 95, 2193). Since then numerous other syntheses have been effected (Rosenmund, Ber. 1910, 43, 306; Ehrlich *et al.* Ber. 1912, 45, 2428; Späth and Sobel, Monatsh. 1920, 41, 77; Kindler *et al.*, Annalen, 1923, 431 226; Arch. Pharm. 1927, 265, 394; 1933, 271 441; Raoul, Compt. rend. 1937, 204, 74 G.P. 233069, 248385).

Hordenine salts have been employed as a remedy in cases of typhoid, dysentery, enteritis etc. For further details of its pharmacology see Rietachel, Arch. exp. Path. Pharm. 1937, 186 387. The *methylurea* derivative of hordenine

shows myotic action (Stedman, Biochem. J. 926, 20, 719). *o*-( $\beta$ -Dimethylaminoethyl) phenol hordenine) has been synthesised by Von Braun and Bayer (Ber. 1924, 57 [B], 193); its physiological action is much weaker than that of oordenine.

Schl.

**HORMONES.** The term hormone denotes a number of physiologically active substances secreted directly into the blood stream or the lymphatic system of animals by various organs named endocrine glands. These internal secretions serve to regulate various functions of the body, often in a part of the body remote from their source, and very small amounts of them in most cases suffice for the purpose.

The deficiency of a given hormone gives rise to characteristic symptoms in the animal—the effect of castration in domestic animals is a familiar example—and these can usually be alleviated or cured by the administration of the pure hormone, or of an extract containing it. The general principle of the biological assay of hormone preparations depends on the production of such effects. The League of Nations Health Organisation (Quart. Bull. Health Organisation, League of Nations, 1935, 4, 618; 1938, 7, 887) has established standards for the sex and pituitary hormones, some of which consist of pure crystalline substances.

Following upon the isolation of the pure hormones, the chemical constitution of a number of them has been determined; the chemistry of the most important hormones is summarised below.

**Hormones of the Pituitary Gland (Hypophysis).**—The *anterior lobe* of the pituitary gland produces a large number of hormones, and appears to act as a central co-ordinating mechanism controlling the secretions of other endocrine glands. The following glands are dependent on pituitary control: pancreas (insulin secretion), thyroid, parathyroid, the sex glands, and adrenal (medulla and cortex); there are also hormones controlling lactation, carbohydrate metabolism apart from insulin secretion, etc. An important function of the pituitary gland is the control of growth, and acromegaly and gigantism, and also insufficient growth are associated with disturbances of the hypophysis.

Of the above hormones, those controlling the sex glands (*gonadotropic hormones*) have been particularly widely studied, although their chemistry has not been elucidated. Two effects on female animals can be distinguished, one the ripening of ovarian follicles, the other the formation of corpora lutea; in the male they produce spermatogenesis and the proliferation of the interstitial cells. Although Zondek has given the names "prolan A" and "prolan B" to the substances responsible for these effects, and materials, exerting mainly one or other of these effects, can be prepared, separation is difficult if not impossible. The beginnings of chemical study are made possible by the fact that pregnant women excrete material with high hormone activity, derived probably from the placenta; it may be noted that this secretion is utilised in the widely used method for the diagnosis of pregnancy in its early stages (Aschheim-Zondek



test). The active material is obtained from urine by precipitation with phosphomolybdic acid, the precipitate is dissolved in ammonia, baryta water added and the hormone precipitated from the filtrate by adding alcohol and ether (G.P. 588047). In U.S.P. 2035642; B.P. 406531, acetone saturated with benzoic acid is added to the hormone solution acid with acetic acid. The precipitate contains the hormone. A later method is the adsorption of the active material on benzoic acid, followed by dialysis and precipitation with tannic acid or other reagents (Gurin, Bachman and Wilson, J. Biol. Chem. 1939, **128**, 525). Another important source of gonadotropic hormones is the serum of pregnant mares, from which a potent preparation can be obtained by removal of the inactive proteins with salicylsulphonic acid, followed by dialysis and precipitation with acetone (Rinderknecht, Noble and Williams, Biochem. J. 1939, **33**, 381). The active material is classed as a mucoprotein and contains a carbohydrate-polypeptide complex.

The secretion of prolans can be influenced by the administration of the sex hormones proper, and a delicate balance between them is maintained in the body (for an account, see Ammon and Dirscherl, "Fermente, Hormone, Vitamine," Leipzig, 1938; Berblinger, "Ergebnisse der Vitamin- und Hormonforschung," I, 191, Leipzig, 1938).

The *posterior lobe* of the pituitary gland is comparatively poor in hormones, which are distinguished as the *pressor* (*pitressin*, *vasopressin*) which causes a rise in blood pressure, the *oxytocic* (*pitocin*) with an effect on the irritability of uterine muscle, and the *melanophoric*, which controls pigmentation in some animals. These hormones have been tolerably well separated from one another and characterised as belonging to the proteins. The same applies to the anterior lobe hormones; their chemistry is otherwise obscure.

**Thyroid Hormone.**—The essential nature of the thyroid hormone has been recognised for a long time; removal of the gland leads to symptoms known as myxedema, whilst goitre and cretinism have been traced to thyroid insufficiency, usually due to an inadequate supply of iodine in the diet. Hyperfunction of the gland, as seen in Graves's disease, leads on the other hand to increase in the metabolic rate accompanied by tachycardia, exophthalmia and nervous symptoms.

The gland contains a gelatinous "colloid," which is a globulin-like protein (thyroglobulin), but it contains a comparatively large amount (0.6%) of iodine; indeed, nearly the whole of the iodine content of the body is concentrated in the thyroid gland in a non-ionisable form.

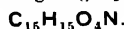
**Extraction.**—The physiologically active iodine-containing portion of the thyroglobulin molecule was isolated by hydrolysis of thyroid gland tissue with sodium hydroxide (Kendall, J. Biol. Chem. 1919, **39**, 125) in the form of the crystalline *thyroxine*,  $C_{15}H_{11}O_4N_1I_4$ , m.p. 231–232°, which has the characteristic physiological activity of the thyroid hormone. The yield of thyroxine was greatly improved by Harington (Biochem. J. 1926, **20**, 293), who used stepwise

hydrolysis with baryta: thyroglobulin (or gland substance) is boiled for 5 hours with 10% aqueous baryta, and the filtered solution acidified; the acid-insoluble portion is re-hydrolysed for 18 hours with 40% baryta at 100°. The insoluble barium salts yield thyroxine, obtained crystalline by acidifying an alkaline alcoholic solution with acetic acid at the boiling-point. Harington and Randall (*ibid.* 1929, **23**, 373) have shown that the acid-soluble portion of the hydrolysate contains 3,5-diiodotyrosine and that this and the thyroxine account for the whole of the iodine content of the gland (*cf.* Meyer, "Fortgeschritte der Chemie Organischer Naturstoffe," II, 103, Vienna, 1939).

**Reactions.**—A few milligrams of thyroxine in aqueous-alcoholic hydrochloric acid give with sodium nitrite a yellow colour which deepens to orange on boiling; addition of ammonia produces a rose-red colour. This test is characteristic of compounds containing the 2,6-diiodophenol grouping and is also given by diiodotyrosine; both compounds also give the ninhydrin reaction (*v. Vol.* I, p. 324b).

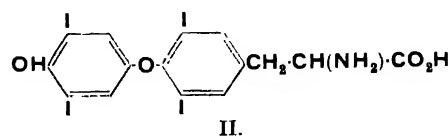
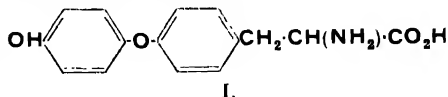
**Biological Assay.**—Estimating the percentage of the alkaline hydrolysate of thyroid gland tissues which is insoluble at  $pH$  5 (Harington) or extractable by butyl alcohol (Leland) is a reasonably accurate method of chemical assay. The biological tests depend on measurements of the increase in metabolism, the diminution of the liver glycogen content or the accelerating effect on the development of tadpoles; the Reid-Hunt test measures the increases in the resistance of thyroid-treated mice to poisoning by acetonitrile.

**Constitution.**—Thyroxine on catalytic reduction loses its iodine, giving *thyronine*,



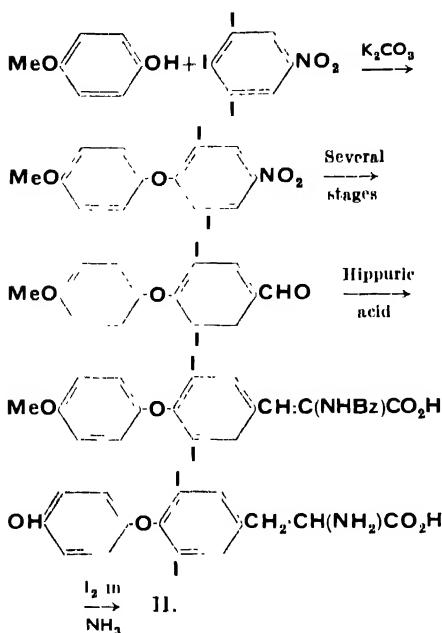
This has been degraded by fusion with potash to oxalic acid, ammonia, *p*-hydroxybenzoic acid, quinol, and a phenol which was shown by synthesis to be *p*-(*p*'-hydroxyphenoxy)-toluene. This, and the degradation of thyronine by exhaustive methylation and graduated oxidation show that it must have the structure (I), which has been confirmed by synthesis (Harington, Biochem. J. 1926, **20**, 300).

Thyroxine itself gives on alkaline fusion products of the pyrogallol type and no *p*-hydroxybenzoic acid, from which it follows that 2 atoms of iodine must be adjacent to the hydroxyl and two more must be in the second ring. This, and the analogy with diiodotyrosine leads to the formula (II) for thyroxine.



This structure is confirmed by the exhaustive methylation and oxidative degradation of thyroxine. The synthesis of thyroxine (Haring-

ton and Barger, *ibid.* 1927, 21, 169) was carried out as follows:



The penultimate stage involves simultaneous demethylation, loss of the benzoyl group and reduction of the double bond.

Thyroxine was resolved (Harington, *ibid.* 1928, 22, 1429) and the *l*-(-) form, m.p. 235–236°,  $[\alpha]_{\text{D}}^{20} -3.5^\circ$  proved to be physiologically somewhat more active than the racemic, which is obtained by the alkaline hydrolysis of thyroid tissue; the active form was later obtained from thyroglobulin by intensive peptic digestion, followed by tryptic digestion (Harington and Salter, *ibid.* 1930, 24, 456). Both it and the physiologically inactive *l*-(-)-diiodotyrosine are constituent amino-acids of thyroglobulin (Cutton, Harington and Yuill, *ibid.* 1938, 32, 1119); in configuration *l*-(-)-thyroxine is related to *l*-(-)-tyrosine (Canzanelli, Harington and Randall, *ibid.* 1934, 28, 68).

The active hormone of the thyroid cannot be thyroglobulin, because thyroid preparations are active when administered by the mouth to thyroidectomised individuals, and in Harington's view it is probably a peptide containing both *l*-(-)-thyroxine and *l*-(-)-diiodotyrosine.

Clinically, thyroid preparations (dried gland or synthetic thyroxine) are used in the treatment of myxoedema and other cases of thyroid insufficiency and also of obesity, owing to their capacity for increasing the metabolism, particularly that of proteins.

**Parathyroid Hormone.**—The parathyroid gland controls the calcium metabolism of the body by means of a special hormone; removal of the gland leads to symptoms known as tetany, which can be alleviated by administration of calcium and of extracts of the gland (Collip). The hormone is not dialysable, it

appears to be akin to insulin, but nothing is known of its chemistry.

**Pancreatic Hormone.**—The hormone of the pancreas is *insulin* (*q.v.*).

**Secretin.**—The mucous membrane of the small intestine gives on extraction with acids a preparation which, when injected into the blood stream, causes a secretion of pancreatic juice (Bayliss and Starling, *J. Physiol.* 1902, 28, 325). The active compound, secretin, is a complex polypeptide of unknown constitution (*cf.* Agren, *J. Physiol.* 1938–39, 94, 553; Niemann, *Proc. Nat. Acad. Sci.* 1939, 25, 267).

**Oestrogenic Hormones.**—Substances capable of inducing the phenomena of oestrus (heat) in ovariectomised animals have been isolated from a variety of sources, but principally ovaries, placenta and pregnancy urine.

**Biological Assay.**—This is generally carried out by the vaginal smear method of Allen and Doisy (*J. Amer. Med. Assoc.* 1923, 81, 819).

**Isolation.**—Pregnancy urine is extracted with ether, the extract evaporated, the residue dissolved in methyl alcohol and shaken with light petroleum. The alcoholic solution is diluted and extracted with ether, the extract again evaporated and subjected to partition between 60% alcohol and benzene. The alcohol solution contains mainly oestriol, the benzene solution oestrone. The crude hormones are subjected to hydrolysis with hydrochloric acid; their ether solution is then freed from acids with sodium carbonate, and extracted with sodium hydroxide. This removes the hormones, leaving the inactive pregnanediol in the ether; the hormones are finally reprecipitated with acid and taken up in ether. Oestrone is distilled in a high vacuum, whilst oestriol is precipitated from an alcoholic solution by means of ether (Butenandt and Hildebrandt, *Z. physiol. Chem.* 1931, 199, 243). A later method (Cohen and Marrian, *Biochem. J.* 1936, 30, 57; Cohen, Marrian and Odell, *ibid.* 2250) involves concentration of the urine to one-eighth and extraction at  $p_{\text{H}}$  2.5–3.0 with butyl alcohol after saturation with salt; the hormones can be extracted with alkalis and purified, the oestriol being obtained as the sodium salt of the glycuronide (*see below*); more usually, this complex is broken up by acid hydrolysis.

Girard and Sandulesco (*Helv. Chim. Acta*, 1936, 19, 1095) describe the isolation of oestrone from the crude concentrate, obtained by solvent extraction of the urine of pregnant mares, with the aid of Girard's reagent T (*q.v.*). The ketonic constituents are isolated in this way and can be further split up into phenolic (oestrone) and non-phenolic compounds by means of alkali.

The first crystalline compound to be isolated by three groups of workers was *oestrone*,<sup>1</sup>  $\text{C}_{18}\text{H}_{22}\text{O}_2$  (Doisy, Veler and Thayer, *Amer. J. Physiol.* 1929, 90, 329; Butenandt, *Naturwiss.* 1929, 17, 879; Dingemans, de Jongh, Kober and Laqueur, *Deut. med. Woch.* 1930, 56, 301) from human pregnancy urine. Later it was found that oestrone is even more abundant in the urine of pregnant mares, in which it

<sup>1</sup> A variety of names were given to the different preparations, such as theelin, folliculin, etc., and there was some uncertainty about their proper formulation, but in the present account these historical details are omitted.

is accompanied by several related compounds, *equilin*, *equilenin* and (?) *hippulin* (Girard, Sandulesco, Fridenson and Rutgers, Compt. rend. 1932, **194**, 909; **195**, 981; Girard, Sandulesco, Fridenson, Gaudefroy and Rutgers, *ibid.* 1932, **194**, 1020), which can be derived from oestrone by the loss of 2 or 4 atoms of hydrogen. Following the observation of Zondek that the urine of stallions also contains oestrogenic material (Nature, 1934, **133**, 209, 494), pure oestrone has been isolated from this source (Deulofeu and Ferrari, Z. physiol. Chem. 1934, **226**, 192; Hausler, Helv. Chim. Acta, 1934, **17**, 531) and from the urine of normal men (Dingemans, Laqueur and Muhlbock, Nature, 1938, **141**, 927); and the occurrence of oestrone in material of purely botanical origin (palm kernel oil) has been shown by Butenandt and Jacobi (Z. physiol. Chem. 1933, **218**, 104).

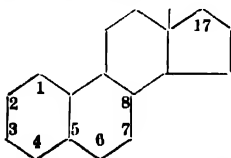
The alcohol *oestriol*,  $C_{18}H_{24}O_3$ , was isolated from human pregnancy urine by Marrian (J.S.C.I. 1930, **49**, 237, 515; Biochem. J. 1930, **24**, 435, 1021) and converted into oestrone by dehydration (Butenandt and Hildebrandt, Z. physiol. Chem. 1931, **199**, 243; Marrian and Haslewood, Biochem. J. 1932, **26**, 25). It was detected in female willow catkins (Skarżyński, Nature, 1933, **131**, 766).

An even more potent oestrogen was isolated from sow's ovaries (McCorquodale, Thayer and Dowsy, Proc. Soc. Exp. Biol. and Med. 1935, **32**, 1182; J. Biol. Chem. 1936, **115**, 435) and proved to be identical with the lower-melting or  $\alpha$ -form of *oestradiol*, the two isomeric forms of which result from the reduction of the carbonyl group of oestrone (Schwenk and Hildebrandt Naturwiss. 1933, **21**, 177; Wintersteiner, J. Amer. Chem. Soc. 1937, **59**, 765). The  $\beta$ -diol, together with the corresponding alcohol derived from equilenin, was found to be a constituent of "8 follicular hormone" obtained from the urine of pregnant mares (Wintersteiner *et al.*, J. Amer. Chem. Soc. 1936, **58**, 2652; J. Biol. Chem. 1937, **119**, cvii).

Water-soluble complexes containing oestriol have been isolated from the placenta and from pregnancy urine (*emmenin* or oestriol glycuronide) and mares' urine (oestrone conjugated with sulphuric acid). Nearly the whole of the oestrogenic material of pregnancy urine is excreted in this combined form, doubtless because the complexes are less toxic to the organism; they exhibit only a fraction of the oestrogenic potency of the hormones themselves when injected into the blood stream, but are almost as potent when administered orally.

**Properties.**—*Oestrone*, 3-hydroxy-17-keto- $\Delta^{1,3,5}$ -oestratriene,<sup>1</sup> crystallises in 3 forms:

<sup>1</sup> The nomenclature is based on the hydrocarbon *estrane*



(Adam, Danielli, Dodds, King, Marrian, Parkes and Rosenheim, Nature, 1933, **132**, 205).

m.p. 254° (rhombic metastable), m.p. 256° (monoclinic metastable) and m.p. 259° (rhombic stable), and has  $[\alpha]_D +170^\circ$  (in dioxan). The *acetate* has m.p. 126°, the *benzoate* m.p. 218–219°, the *methyl ether* m.p. 168.5–169°, the *oxime* m.p. 241–242° (corr.), the *semicarbazone* ( $+ \frac{1}{2} H_2O$ ) m.p. 266–267° (corr.). 0.1  $\mu$ g. of oestrone constitutes one international unit of oestrogenic activity.

$\alpha$ -*Oestradiol*, 3:17-dihydroxy- $\Delta^{1,3,5}$ -oestratriene, has m.p. 176–178° (corr.),  $[\alpha]_D +81^\circ$  (in alcohol); the *3-acetate* has m.p. 136.5–137.5°, the *17-acetate*, m.p. 215–217.5° (corr.) and the *diacetate* m.p. 127°. The physiological activity of  $\alpha$ -oestradiol is higher than that of oestrone and is enhanced by esterification (Miescher, Scholz and Tschopp, Biochem. J. 1938, **32**, 725).

$\beta$ -*Oestradiol* has m.p. 220–223° (corr.),  $[\alpha]_D +54^\circ$  (in dioxan; the *diacetate* has m.p. 139–141.5° (corr.).

*Oestriol*, 3:16:17-trihydroxy- $\Delta^{1,3,5}$ -oestratriene, has m.p. 281° (corr.),  $[\alpha]_D +61^\circ$  (in alcohol); the *triacetate* has m.p. 126°, the *methyl ether* m.p. 162.5–164° (corr.).

*Equilin*, 3-hydroxy-17-keto- $\Delta^{1,3,6,7}$ -oestratriene, has m.p. 238–240°,  $[\alpha]_D +308^\circ$  (in dioxan); the *benzoate* has m.p. 197–198°, the *methyl ether* m.p. 160.5–161.5°.

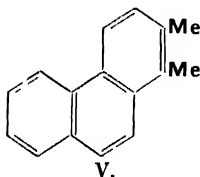
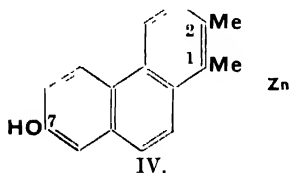
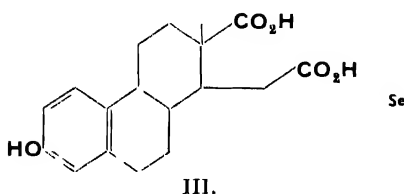
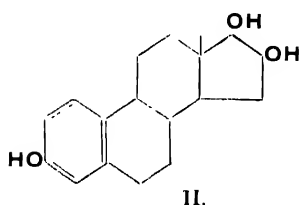
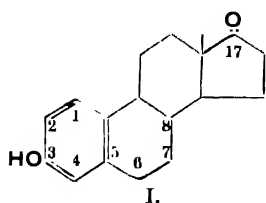
*Hippulin* has m.p. 233° (corr.),  $[\alpha]_D +128^\circ$  (in dioxan).

*Equilenin*, 3-hydroxy-17-keto- $\Delta^{1,3,5,6,8}$ -oestratriene, has m.p. 258–259° (corr.),  $[\alpha]_D +87^\circ$  (in dioxan), and forms an *acetate*, m.p. 156–157°, a *benzoate*, m.p. 222–223° (corr.) and a *methyl ether*, m.p. 197–198° (corr.).

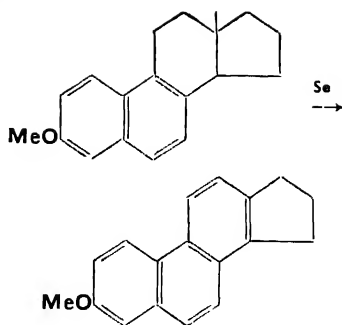
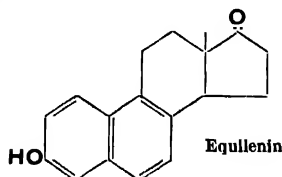
**Colour Reactions.**—The natural oestrogens give with sulphuric acid an orange colour (Marrian), with a fluorescence which is green with oestrone and oestriol, blue with oestradiol (Schwenk and Hildebrandt). Kober modified this test by adding phenol to the acid, and several colorimetric methods of estimation were based on this test (Cohen and Marrian, *ibid.* 1934, **28**, 1603; Pincus, Wheeler, Young and Zahl, J. Biol. Chem. 1936, **116**, 253; Zimmermann, Klin. Woch. 1938, **17**, 1103); the most useful of these is Kober's modified test, using  $\alpha$ -naphthol in place of phenol (*cf.* Biochem. J. 1938, **32**, 357).

**Constitution.**—The structure of oestrone was ascertained as follows: the general type of ring structure and the presence of two active groups at opposite ends of the molecule were deduced from a crystallographic study of oestrone and oestriol by the X-ray method (Bernal, J.S.C.I. 1932, **51**, 259), and by an examination of their monomolecular films (Adam, Danielli, Haslewood and Marrian, Biochem. J. 1932, **26**, 1233). Marrian and Haslewood (J.S.C.I. 1932, **51**, 277) suggested a structure based on that of the sterols, which was further elaborated to (I) by Butenandt (Nature, 1932, **130**, 238) and this was confirmed by later work. Thus, oestriol (II) gives on fusion with potash the acid (III) (Marrian and Haslewood, *l.c.*), which is dehydrogenated by selenium to the phenanthrol (IV) and the latter is converted into 1:2-dimethylphenanthrene (V), identical with  $\alpha$

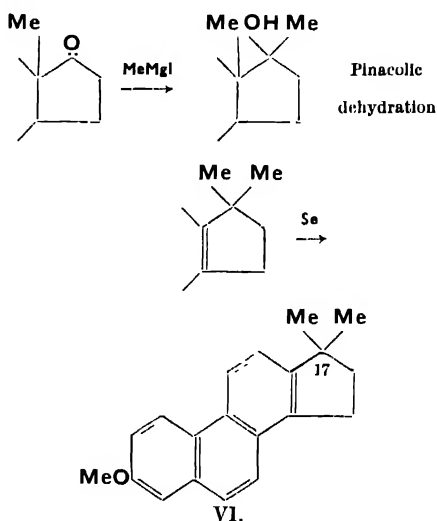
synthetic specimen (Butenandt, Weidlich and Thompson, Ber. 1933, **66**, [13], 601):



Later, 1:2-dimethyl-7-phenanthrol was synthesised by Haworth and Sheldrick (J.C.S. 1934, 864). Final proof of the skeleton assigned to oestrone and equilenin was afforded by Cook and Girard (Nature, 1934, **133**, 377) and Cohen, Cook, Hewett and Girard (J.C.S. 1934, 653) by converting the methyl ethers of these compounds, after reduction of the ketone group, into the same methoxy-compound, which was synthesised:



The position of the ketone grouping was proved as follows:



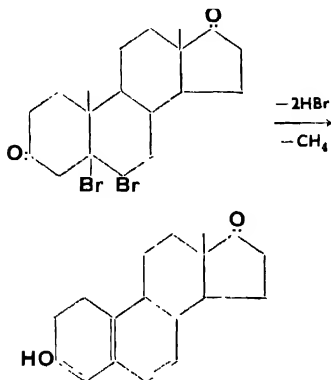
(Cohen, Cook and Hewett, *ibid.* 1935, 445). A similar pinacolic migration occurs when oestradiol methyl ether is dehydrated: the product on dehydrogenation gives a methoxy-compound analogous to (VI), but with only one methyl group in position 17.

Equilin has been dehydrogenated to equilenin with palladium black, showing that the skeleton and the position of the functional groups are the same (Dirschel and Hanusch, Z. physiol. Chem. 1935, **233**, 13; **236**, 131); as the absorption spectrum of equilin is similar to that of more oestrone, the additional double bond is not conjugated with those of the benzene ring and probably occupies the position 7:8 (Cook and Roe, J.S.C.I. 1935, **54**, 501).

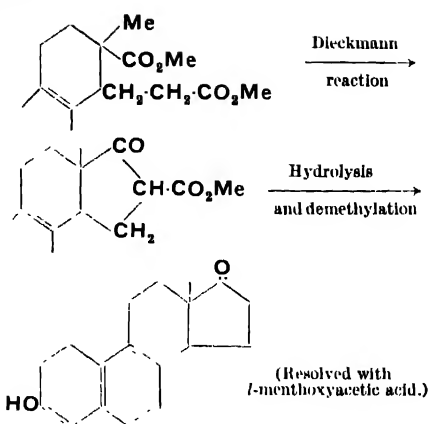
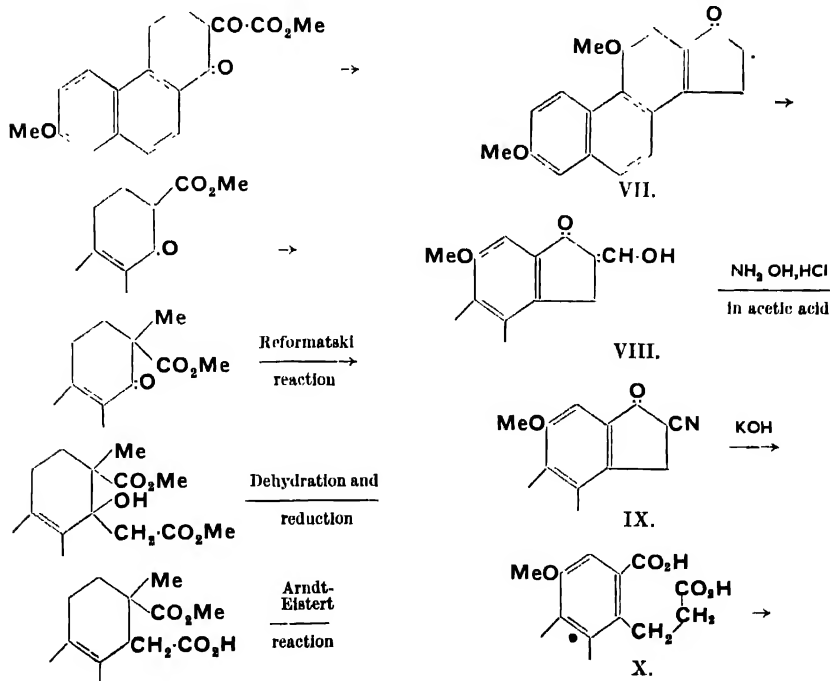
*Origin of the Estrogens.*—Following Butenandt, it is commonly assumed that the oestrogens are formed in the body by a degradation of cholesterol involving the removal of the side-chain and partial dehydrogenation of the resulting compound. This view receives support from the definite oestrogenic activity of testosterone and *iso*androstenediol, which might be expected to undergo such a dehydrogenation in the body; it is also in keeping with the occurrence of

- androgenic substances in the ovary and of oestrogens in the testis, but is nevertheless purely speculative. The metabolism of steroid hormones generally is discussed by Marker (J. Amer. Chem. Soc. 1938, **60**, 1725).

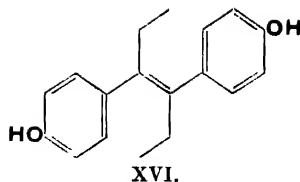
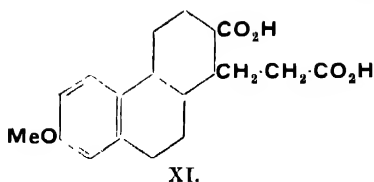
*Synthesis of Oestrogens.*—A feebly oestrogenic compound was prepared by heating the debromination product of dibromoandrosterone, when a phenolic substance was produced with loss of methane; the substance is *isoequilin*, m.p. 252°,  $[\alpha]_D +170^\circ$ , and may perhaps be identical with hippulin (Inhoffen, Naturwiss. 1937, **25**, 125):



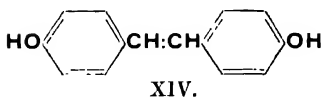
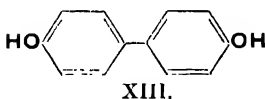
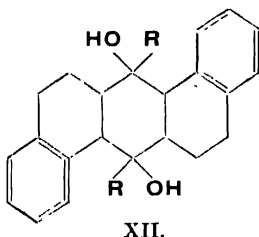
The synthesis of equilin has been announced, although full details are not yet available, by Bachmann, Cole and Wilds (J. Amer. Chem. Soc. 1939, **61**, 974), who used the following route:



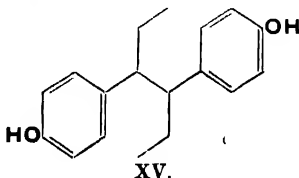
The synthesis of a compound having the skeleton structure of equilin, but lacking the angular methyl group, has been achieved by Koebner and Robinson (J.C.S. 1938, 1994), this is termed *x-norequilin* to denote that the stereo-chemical configuration of the compound is unknown. An analogous *x-norestrone* has also been prepared by Robinson and Rydon (*ibid.* 1939, 1394); the compound (VII) was synthesised by the method of Robinson (*ibid.* 1938, 1390), but it could not be reduced direct to *norestrone*, although *norequilin* was prepared in this way. The five-membered ring was therefore opened by way of the steps (VIII) and (IX) and the resulting compound hydrogenated in several stages. The final product (XI) gave *norestrone* methyl ether on cyclisation:



**Artificial Oestrogens.**—Apart from the synthesis of the natural oestrogenic compounds, a vast number of potentially active compounds have been prepared and tested. The first compound with a measurable activity was 1-keto-1:2:3:4-tetrahydrophenanthrene (Cook, Dodds and Hewett, *Nature*, 1933, **131**, 56). A series of dialkyl-dihydroxy-compounds of the type (XII) was prepared and the dipropyl compound ( $R=C_3H_7$ ) found to have an activity comparable with that of oestriol; some other members of the series were also active (Cook, Dodds, Hewett and Lawson, *Proc. Roy. Soc.* 1934, B, **114**, 272). The phenanthrene skeleton present in these compounds and in the natural oestrogens is not, however, essential for activity, for *pp'*-dihydroxydiphenyl (XIII) and *pp'*-dihydroxystilbene (XIV) are active.



Recently a compound, of the formula (XV), with a potency approximately equal to that of  $\alpha$ -oestradiol was found in the by-product of the demethylation of anethole (Campbell, Dodds and Lawson, *Nature*, 1938, **141**, 78), and an equally active compound is the corresponding stilbene, "diethylstilboestrol" (XVI) (Dodds, Golberg, Lawson and Robinson, *Proc. Roy. Soc.* 1939, B, **127**, 140); this produces 100% response in doses of 0.0004 mg. when tested on spayed rats.



A stereoisomeride, thought to be the *cis*-compound (*ψ*-diethylstilboestrol), has only one-tenth the activity of (XVI). The latter is the most active of a series of homologues which have been prepared and tested; another compound of comparable potency is 4:4'-dihydroxy- $\gamma\delta$ -diphenyl- $\Delta^{\beta\delta}$ -hexadiene, which also has a chain of 6 carbon atoms.

Diethylstilboestrol can be administered orally or subcutaneously, and shows all the biological properties of the natural oestrogens; it confers the mating instinct on ovariectomised animals, sensitizes the rabbit uterus to progesterone, and acts on the anterior lobe of the pituitary gland.

The duration of oestrus induced by diethylstilboestrol is brief, but may be prolonged by administering it in the form of esters (propionate), just as is the case with oestradiol.

#### Corpus Luteum Hormone (Progesterone).

—The corpus luteum of the mammalian ovary produces a hormone indispensable to pregnancy. This causes characteristic changes in the mucous membrane of the uterus: the mucous membrane proliferating as the result of the action of oestrogenic hormones is changed into a secreting membrane, and thus adapted for the reception of the fertilised ovum; the hormone also assists in the maintenance of pregnancy, and the removal of the corpus luteum during that period causes the ejection or absorption of the developing ovum. Later in pregnancy the placenta takes over the task of supplying the hormone. The oestrogenic hormones are in some respects inhibitory of the physiological activity of progesterone.

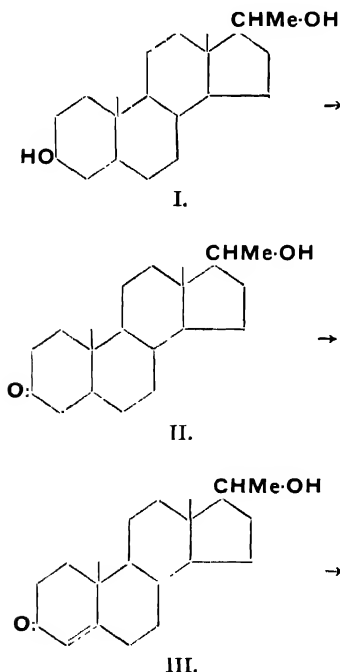
**Biological Assay.**—The assay of the hormone is based on the changes it produces in the uterus of a rabbit previously treated with oestrogens (Allen and Corner test); the preliminary proliferation of the endometrium can be induced in an immature rabbit by administration of oestrone (Clauberg test). An international unit is equal to 1 mg. of progesterone.

**Extraction.**—Sow's ovaries (or corpora lutea) are the best source of the hormone. These are generally extracted with alcohol, the solvent is removed and the residue taken up in ether; phospholipoids are precipitated with acetone, cholesterol and fats are frozen out from a methyl alcohol solution, acids are removed with sodium bicarbonate; oestrone may be eliminated by partition between light petroleum and alcohol (Corner and Allen, *Amer. J. Physiol.* 1929, **88**, 326; Allen, *ibid.* 1930, **92**, 174; *J. Biol. Chem.* 1932, **98**, 591; Allen and Meyer, *Amer. J. Physiol.* 1933, **106**, 55). The final step in the purification is carried out with carbonyl reagents. The yield is about 50 mg. from 100 kg. of ovaries.

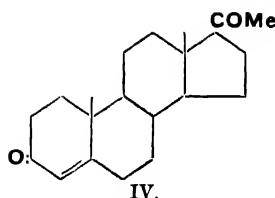
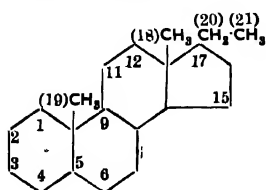
The pure crystalline hormone, *progesterone*,

was isolated by four independent groups of workers (Butenandt, Westphal and Hohlweg, *Z. physiol. Chem.* 1934, **227**, 84; Slotta, Ruschig and Fels, *Ber.* 1934, **67** [B], 1270; Allen and Wintersteiner, *Science*, 1934, **80**, 190; Hartmann and Wettstein, *Helv. Chim. Acta*, 1934, **17**, 878, 1365). It is an unsaturated diketone  $C_{21}H_{30}O_2$  and occurs in two polymorphic varieties, m.p.  $128^\circ$  and  $121^\circ$ ,  $[\alpha]_D +187^\circ$ ; it is accompanied by the physiologically inert *allopregnanol-20-one*.<sup>1</sup>

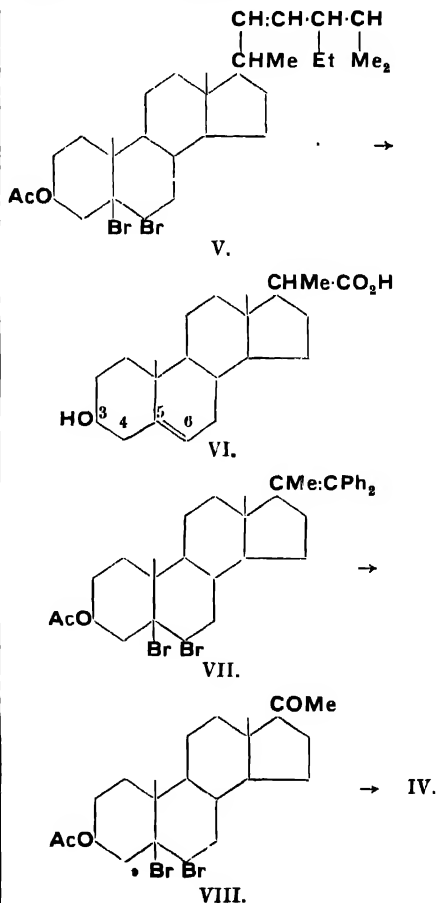
**Constitution.**—The constitution of progesterone was at first deduced by analogy and finally confirmed by syntheses. The first of these starts from pregnanediol (I), a physiologically inactive compound which is found in pregnancy urine, and may be produced from progesterone in the course of metabolism. It is converted by partial oxidation into the keto-alcohol (II), which gives the unsaturated compound (III) by bromination and removal of hydrobromic acid; gentle oxidation then gives progesterone ( $\Delta^4$ -pregnene-3:20-dione) (IV) (Butenandt and Schmidt, *Ber.* 1934, **67** [B], 1893, 1901):



<sup>1</sup> The nomenclature is based on the hydrocarbon pregnane or 17-ethylandrosterane.



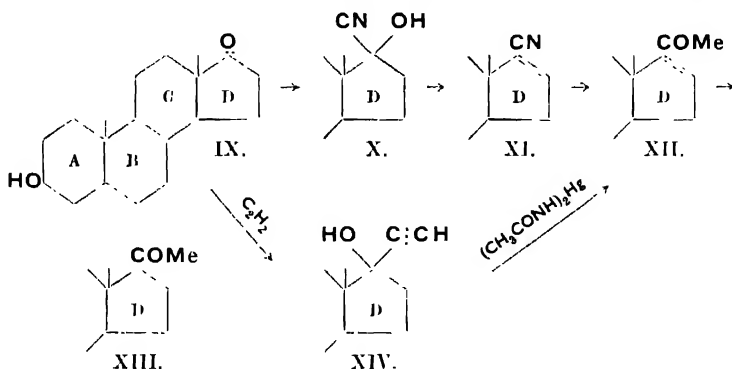
Another synthesis (Fernholz, *ibid.* 1934, **67** [B], 1855; Fernholz and Chakravarti, *ibid.* 1935, **68** [B], 353) starts from a vegetable material, stigmasterol, the acetate of which is ozonised after protecting the nuclear double bond by bromination (V); the product is debrominated and hydrolysed to 3-hydroxybisanorcholenic acid (VI). The side-chain is then shortened by the action of phenyl magnesium bromide on the ester and oxidation of the acetate of the product, the double bond being again protected by bromination (VII). The acetate (VIII) is hydrolysed to the alcohol, which is oxidised to the ketone and the latter debrominated to progesterone, the double bond migrating spontaneously into the  $\Delta^4$ -position:



This process is used for the large-scale preparation of progesterone, which is in great demand for clinical purposes, but many attempts have recently been made to devise a synthesis from readily available starting materials. Thus, cholestenone has been oxidised with chromic acid to a mixture of progesterone and androstenedione, although the yields are not stated (Dürscherl and Hanusch, *Z. physiol. Chem.* 1938, **252**, 49). In the more recent syntheses the comparatively accessible  $C_{19}$  compounds of the androstene series are converted into  $C_{21}$  compounds. In one of these (Butenandt and

Schmidt-Thomé, *Ber.* 1939, **72** [B], 182) *trans*-dehydroandrosterone (IX) (see p. 275a) is converted into the cyanhydrin, which is dehydrated and the unsaturated nitrile treated with methyl magnesium bromide. The product (XII) is reduced to the compound (XIII) without reducing the double bond in ring B. The final oxidation of the hydroxyl in ring A is achieved by a modification of the Oppenauer method with aluminium isopropoxide and cyclohexanone, which brings about the migration of the double bond into ring A at the same time.

The compound (XII) has also been obtained



(Goldberg and Aeschbacher, *Helv. Chim. Acta*, 1939, **22**, 1185) by the addition of the elements of water to the condensation product of *trans*-dehydroandrosterone and acetylene (XIV) (Ruzicka and Hofmann, *ibid.* 1937, **20**, 1280); the reagent used was mercury acetamide in alcohol, the mercury complex formed being decomposed with hydrogen sulphide. Other methods bring about enlargement of the five-membered ring. Two other syntheses (Butenandt, Schmidt-Thomé and Paul, *Ber.* 1939, **72** [B], 1112; Miescher and Kägi, *Helv. Chim. Acta*, 1939, **22**, 184) are chiefly of academic interest.

Progesterone, unlike œstrone, is highly specific in its action and is completely inactivated by reduction of the double bond; some derivatives of testosterone alkylated in the 17-position possess, however, some degree of activity (Klein and Parkes, *Proc. Roy. Soc.* 1937, B, **121**, 574).

**Androgenic Hormones.**—Substances with male hormone activity have been isolated from vertebrates only, although certain plant extracts are said to exhibit androgenic activity (Loewe). Early experiments showed that materials were formed in the testicles which were indispensable for the proper functioning of the male genital organs and the preservation of the secondary sex characteristics; without them the well-known phenomena accompanying castration are observed. Active extracts of testes were obtained by F. C. Koch, C. R. Moore and their collaborators; the presence of active material in urine was demonstrated by Loewe and Voss and by Funk.

**Biological Assay.**—The increase in growth of a capon's comb under the influence of androgenic materials was first utilised as a quantitative test by Gallagher and Koch (1929) and adopted at

the London Conference for the Standardisation of Sex Hormones in 1935; a "capon unit" is equal to 100  $\mu$ g. of androsterone. Another test depends on the increase in the size of seminal vesicles in castrated rodents (Loewe and Voss, Korenchevsky); the two tests do not always give equivalent results (for a detailed account, see F. C. Koch, "The Male Sex Hormones," *Physiol. Reviews*, 1937, 17).

**Isolation.**—Lipoid-soluble active bodies have been isolated from testes and human urine, of men or castrates, and even from the female organism. It was eventually found that the activity of extracts of male urine was due to androsterone (Butenandt, *Z. angew. Chem.* 1931, **44**, 905; 1932, **45**, 655; *Nature*, 1932, **130**, 238; Butenandt and Tscherning, *Z. physiol. Chem.* 1934, **229**, 167, 185) and that of testes extracts to testosterone (Laqueur, David, Dingemans and Freud, *Acta brev. neerl.* 1935, **5**, 84; *Z. physiol. Chem.* 1935, **233**, 281); *trans*-dehydroandrosterone, about one-third as active as androsterone, was isolated from urine by Butenandt and Dannenbaum (*Z. physiol. Chem.* 1934, **229**, 192; Butenandt, Dannenbaum, Hanisch and Kudzusz, *ibid.* 1935, **237**, 57) and it was found that adrenosterone, from adrenal cortex (p. 278b), possesses androgenic activity.

The method of extraction of androsterone from male urine was similar to that employed for œstrone (p. 268c), except that androsterone is not phenolic and is therefore found in the neutral portion of the extract. As a method of preparation this process has been superseded by the synthetic method described on p. 275a.

**Properties.**—*Cis*-androsterone has m.p. 184–185° (corr.),  $[\alpha]_D^{25} +94.6^\circ$  (in alcohol), the acetate m.p. 164.5–165.5° (corr.), the oxime

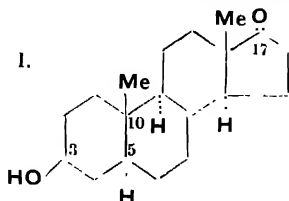


m.p. 209–211° (corr.), the *semicarbazone* m.p. 276° (corr.). 100 $\mu$ g. equal 1 International unit.

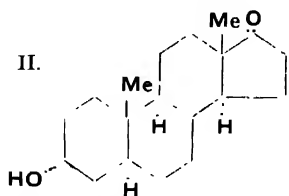
*Trans*-testosterone has m.p. 154.5–155.5° (corr.),  $[\alpha]_D +109^\circ$  (in alcohol), the *acetate* m.p. 140–141° (corr.), the *propionate* m.p. 121–123° (corr.), the *benzoate* m.p. 198–200° (corr.). 15 $\mu$ g. equal 1 International unit.

*Trans*-dehydroandrosterone occurs in two forms, m.p. 140–141° (corr.) and 152–153° (corr.),  $[\alpha]_D +10.9^\circ$  (in alcohol), the *oxime* has m.p. 188–189°, the *acetate* m.p. 171–172° (corr.). 200 $\mu$ g. equal 1 International unit.

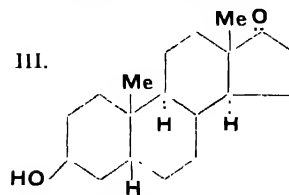
*Constitution*.—The amount of androsterone isolated by Butenandt and Tscherning (*ibid.* 1934, 229, 167, 185) was barely sufficient to establish the formula as  $C_{19}H_{30}O_2$  and the correct constitution was put forward by analogy with that of oestrone. This and the configuration of the compound were established by the synthesis of androsterone by Ruzicka, Goldberg and Brüngger (Helv. Chim. Acta, 1934, 17, 1380) and Ruzicka, Goldberg, Meyer, Brüngger and Eichenberger (*ibid.* p. 1395). They oxidised the acetates of cholestanol, coprosterol and their *epi*-compounds with chromic acid and obtained the acetates of four stereoisomeric hydroxyketones:



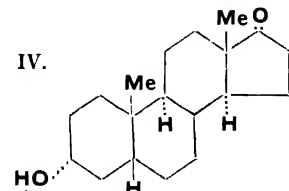
From cholestanol (*iso*androsterone), m.p. 175–176°.



From *epi*cholestanol (androsterone), m.p. 184°.



From coprosterol, m.p. 150–151°.

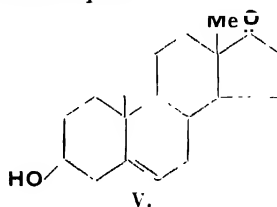


From *epi*coprosterol, m.p. 152–153°.

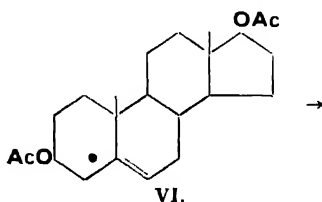
(M.p.'s are corrected.)

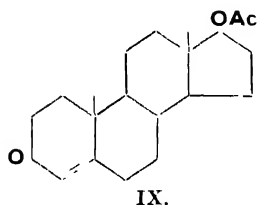
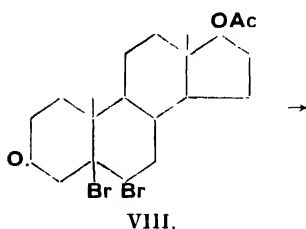
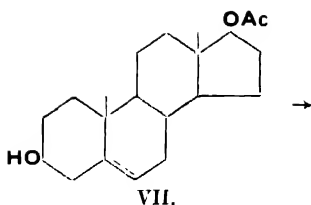
Of these, (II) 3-*epi*hydroxy $\Delta^5$ choleholane-17-one proved to be identical with androsterone; *iso*- or *trans*-androsterone (I) showed one-eighth the activity of androsterone in the capon test and (III) and (IV) were inactive; the great importance of the stereochemical configuration will be noted. Androsterone is prepared on the large scale by the above method.

Oxidation of dibromcholesteryl acetate Ruzicka and Wettstein, *ibid.* 1935, 18, 986; Butenandt, Dannenbaum, Hanisch and Kudzus, *ibid.*; Wallis and Fernholz, J. Amer. Chem. Soc. 1935, 57, 1379, 1564) and debromination of the product gives *trans*-dehydroandrosterone (V); the configuration of the hydroxyl group in this compound is like that of *iso*androsterone (for nomenclature, v. Schonheimer and Evans, J. Biol. Chem. 1936, 114, 567). In accordance with this configuration, the compound is precipitated with digitonin, whereas androsterone is not. *Cis*-dehydroandrosterone has been prepared, and is biologically more active than the natural *trans*-compound.



*Testosterone*, isolated from testes proved to be different from these; it was unsaturated and hence unstable to alkali and permanganate and was much more active than androsterone in the rat test (Laqueur *et al.*, *ibid.*; Callow and Deaneley, *Lancet*, 1935, ii, 77). It was isolated in minute amount from the testes of steers (David, Dingemans, Freud and Laqueur (Z. physiol. Chem. 1935, 233, 281) and proved to be an  $\alpha\beta$ -unsaturated ketone,  $C_{19}H_{28}O_2$ ; on careful oxidation it gave  $\Delta^4$  androstene-3:17-dione, also obtained by the oxidation of *trans*-dehydroandrosterone (David, *Acta brev. neerl. Physiol.* 1935, 85, 108). It was then synthesised from the above compound (Ruzicka and Wettstein, *Helv. Chim. Acta*, 1935, 18, 1264; Butenandt and Hanisch, *Ber.* 1935, 68 [B], 1859; Z. physiol. Chem. 1935, 237, 89) by reduction to androstenediol, the acetate of which (VI) can be hydrolysed to a monoacetate (VII), the acetyl group in ring A being removed before that in ring D. After protecting the double bond by bromination the monoacetate was oxidised to (VIII) and on removing bromine testosterone acetate (IX) was obtained:





Testosterone when injected in oil solution is about 7 times more active than androsterone in the capon test. In the rat test its activity is increased by the presence of an acidic material (Laqueur's "X-Stoff") in extracts of testes, probably fatty acids, which have no effect in the capon test. This increased activity is probably connected with the rate of absorption of the active material. Similarly, the activity of testosterone and androsterone can be enhanced by esterification with fatty acids up to valeric acid; testosterone valerate is 10 times more active than testosterone in the rat test, but not in the capon test. Testosterone propionate has the highest activity of any known substance in both tests. Modern theory inclines to the view that testosterone is the only natural androgenic compound and that androsterone is probably a secondary product derived from it (N. H. Callow, *Biochem. J.* 1939, **33**, 559; Dorfman, Cook and Hamilton, *J. Biol. Chem.* 1939, **130**, 285).

A very large number of derivatives of these compounds have been prepared by varying the groups attached to the carbon atoms 3 and 17 in androsterone and testosterone. A number of these compounds have been found to possess considerable biological activity, which is also closely bound up with their stereochemical configuration; a discussion of them is beyond the scope of this article, but reference may be made to a review by Goldberg in "Ergebnisse der Vitamin- und Hormonforschung," Leipzig, 1938, I, 391; see also Ammon and Dirscherl, "Fermente, Hormone, Vitamine," Leipzig, 1938.

A number of androstane derivatives, par-

ticularly unsaturated compounds, have some biological activity as female sex hormones and, on the other hand, oestrogens have a stimulating effect on certain of the male sexual organs. The physiological significance of this is uncertain, but reference may be made to Korenchevsky,

"Ergebnisse der Vitamin- und Hormonforschung," Leipzig, 1938, II, 420, for a discussion of the subject. Some male hormone activity may be derived from the adrenal cortex (see below) and it is known that tumours of the adrenal cortex in women may lead to virilisation; an abnormally high secretion of *trans*-dehydroandrosterone has also been observed in such cases.

**Adrenal Hormones.**—The adrenal gland consists of two parts, the medulla and the cortex. The former secretes adrenalin (*q.v.*). The cortex is essential to life and, in man, atrophy or destruction of this part of the gland is the cause of Addison's disease. Removal of the gland is rapidly fatal, especially in birds, and gives rise to the following symptoms: disturbances of the equilibrium between potassium and sodium in the blood as well as in the amount of water in the blood, adynamia (ready onset of muscular fatigue), difficulty in the assimilation of fats and in the absorption of carbohydrates. It is thought that the last two processes are connected with phosphorylation (Verzar) and that this process is controlled by the adrenal hormones. These deficiency symptoms are relieved by extracts of the adrenal gland, the composition of which has been intensively studied in recent years.

**Biological Assay.**—In the survival test (Cartland and Kuizenga) adrenalectomised animals (rats) are kept alive by injections of the material to be examined. The dog test (Piffner, Swingle and Vars) similarly measures the amount of hormone preparation necessary to maintain a dog in good condition. The muscle fatigue test (Everse and de Fremery) measures quantitatively the diminished resistance to muscle fatigue in rats; the Ingle test is similar, also the swimming test (Gaarenstrom, Waterman and Laqueur). The glucose test is based on the absorption of glucose in rats.

**Isolation.**—The separation of the cortex from the medulla of the adrenal gland is not practicable on a large scale, and whole glands are used; the inactivation of the hormones by heat and alkali must also be borne in mind.

The glands are extracted with alcohol at room temperature, the extract is evaporated, the residue taken up in benzene, then in acetone; after partition between 70% alcohol and hexane the alcoholic layer is filtered through "permutite" to remove adrenalin (losses are sometimes experienced at this stage), evaporated, the residue taken up in water to precipitate resins and again reprecipitated from an alcoholic solution. The yield at this stage is equivalent to 60 g. of dry material from 1,000 kg. of gland (from some 20,000 head of cattle) and contains 1–2 million dog units (Swingle and Piffner, *Amer. J. Physiol.* 1931, **96**, 153, 164, 180; Piffner, Vars and Taylor, *J. Biol. Chem.* 1934, **106**, 625; Piffner and Vars, *ibid.* p. 645). An alternative method (Cartland and Kuizenga,

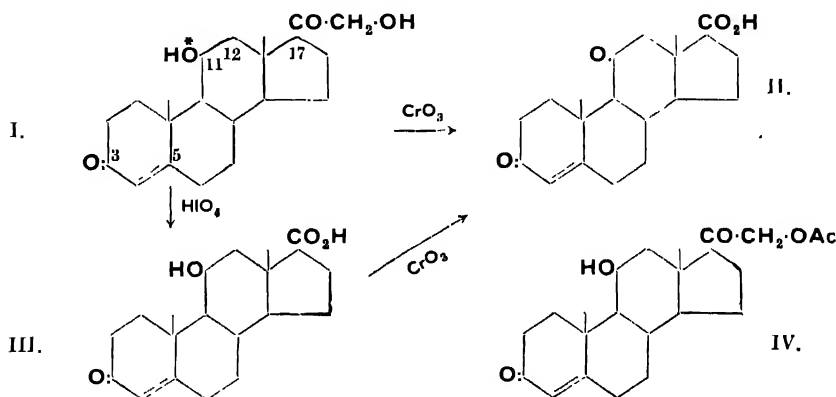
*ibid.* 1936, 116, 57) involves extraction of the glands with acetone, two partitions between 70% alcohol and petroleum and an extraction with ethylene dichloride; the yield of (dry) material is somewhat less (18 g. from 1,000 kg.) but the total activity is higher (2.5 million dog units).

The active material is soluble both in water and in solvents such as ether and benzene and the further purification of the hormones is based on repeated partition between solvents; this has been employed by three groups of workers, namely those of Kendall, Wintersteiner and Pfiffner, and Reichstein. The final isolation of the pure compounds is carried out with carbonyl reagents; Girard's reagent has been particularly valuable in Reichstein's hands. In this way 5 pure active compounds have been isolated, together with 7 or 8 closely related but inactive ones; nevertheless, the amorphous, water-soluble material remaining in the residues appears to be more active than any of the pure compounds hitherto isolated.

Chemically, all the pure compounds found in the adrenal cortex belong to the sterol group;

those which are saturated belong to the cholesterol type and are characterised by an oxygen atom (in addition to one on  $C_3$ ), the position of which is almost certainly on  $C_{11}$ , although this has not yet been strictly proved. They also have an oxygenated side-chain of varying length on  $C_{17}$ .

**Properties and Constitution.**—Corticosterone,  $\Delta^4$ -pregnene-11:21-diol-3:20-dione(I),  $C_{21}H_{30}O_4$ , has m.p. 180–182° (corr.),  $[\alpha]_D +223^\circ$  (in alcohol) (Reichstein, Laqueur, Uylert, de Fremery and Spanhoff, Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 1218; Nature, 1937, 139, 26); it forms an alcoholate, reduces ammoniacal silver solutions and gives the characteristic spectrum of an  $\alpha\beta$ -unsaturated ketone. Oxidation with chromic acid gives the acid (II) (Reichstein, Helv. Chim. Acta, 1937, 20, 953). The hydroxylic nature of the oxygen atom \* (originally placed on  $C_{12}$ ) was recognised by Kendall, Mason, Hoehn and Mackenzie (Proc. Staff Meet. Mayo Clinic, 1937, 12, 136), who showed that the acid (III) was produced by oxidation of corticosterone (I) with periodic acid and (III) could be further oxidised to (II) :



Corticosterone forms a monoacetate (IV) which can be oxidised by chromic acid in the same way, the product being identical with the acetate of dehydrocorticosterone (below).

The position of the side-chain on  $C_{17}$  has been proved by conversion of corticosterone into allopregnone (Steiger and Reichstein, Nature, 1938, 141, 202; Helv. Chim. Acta, 1938, 21, 161).

Corticosterone possesses a high degree of cortin activity, 1 mg. being equivalent to 50–100 g. of suprarenal gland; its esters are equally active, but the activity is almost completely destroyed by the reduction of the double bond.

**Dehydrocorticosterone**,  $C_{21}H_{28}O_4$ , m.p. 174–181.5°,  $[\alpha]_D +299^\circ$  (acetate, m.p. 178–180.5°), has been isolated by Mason, Myers and Kendall (J. Biol. Chem. 1936, 114, 613) and prepared by Reichstein by the oxidation of corticosterone acetate and hydrolysis; it gives the acid (III) on oxidation with either periodic or chromic acid. Its biological activity is inferior to that of corticosterone and it differs from the latter in

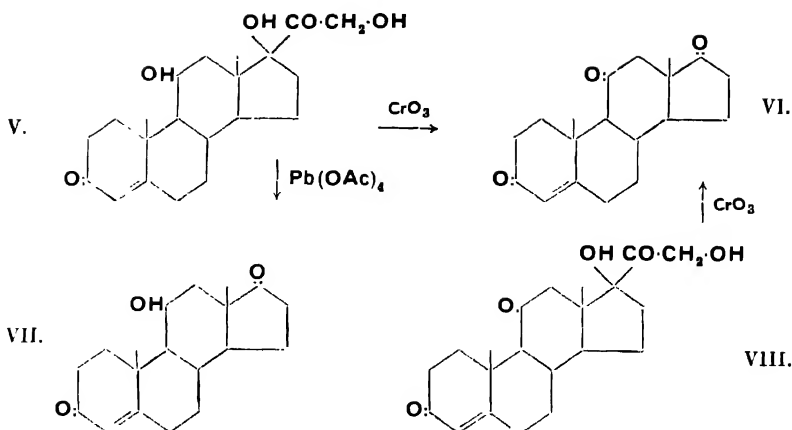
not giving the characteristic green fluorescence with sulphuric acid.

$\Delta^4$ -Pregnene-11:17:21-triol-3:20-dione (V),

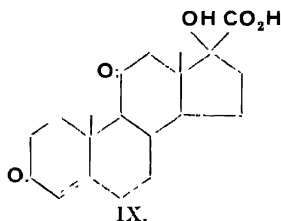


m.p. about 207–210°,  $[\alpha]_D +167.2^\circ$  (Reichstein, Helv. Chim. Acta, 1937, 20, 1164) has some activity in the Everse and de Fremery test, reduces silver solutions and gives a green fluorescence with sulphuric acid. On oxidation with chromic acid it gives adrenosterone (VI), whereas lead tetra-acetate gives the hydroxy-ketone (VII); the acetate of (V), m.p. 223–225°, passes on mild oxidation into the acetate of the compound (VIII) described at the top of the next page.

$\Delta^4$ -Pregnene-17:21-diol-3:11:20-trione (VIII),  $C_{21}H_{28}O_5$ , m.p. about 208°,  $[\alpha]_D +209^\circ$ , was first isolated by Wintersteiner and Pfiffner (J. Biol. Chem. 1935, 111, 585; 1936, 114, lxxx; 116, 291). It is very similar to the triol (V), but can be distinguished by its crystalline form (shining rhombohedra); it has a bitter taste.



Oxidation with chromic acid gives adrenosterone and with periodic acid the hydroxyacid (IX):



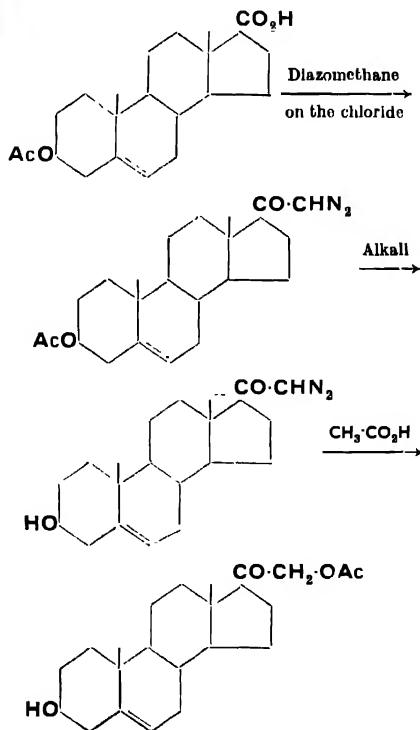
Its activity is somewhat less than that of (V).

*Adrenosterone*,  $\Delta^4$ -androsterone-3:11:17-trione (VI),  $\text{C}_{21}\text{H}_{34}\text{O}_3$ , was isolated from the portions of the adrenal extract more soluble in ether and petroleum by Reichstein (Helv. Chim. Acta, 1936, 19, 29) and has m.p.  $222^\circ$ ,  $[\alpha]_D^{25} + 262^\circ$ ; it has no cortin activity but a considerable androgenic activity (about one-fifth that of androsterone in the capon test) and this provided a clue to its structure. It is hydrogenated to a saturated triketone, m.p.  $178^\circ$ , which has been reduced by Clemmensen's method to androstane, thus fixing the ring structure present in this, and hence also in the other compounds of the group which have been correlated with it. A by-product of the reduction is 17-androstanol, which fixes the position of the side-chain in these compounds, whilst the position of one oxygen atom on  $\text{C}_3$  follows from the fact that the hydroxylated compounds of this series are precipitated by digitonin.

In addition to the above compounds, a number of physiologically inert compounds have been isolated; these have proved useful in elucidating the chemistry of the whole group, and an account of them by Reichstein will be found in "Ergebnisse der Vitamin- und Hormonforschung," Leipzig, 1938, I, 334.

A synthetic compound possessing an even greater biological activity than corticosterone (5 to 7 times greater in the dqg test and about 10 times greater in the Everse and de Fremery test) is deoxycorticosterone or 21-hydroxypro-

gesterone, m.p.  $141-142^\circ$  (corr.),  $[\alpha]_D^{25} + 178^\circ$  (Reichstein and Steiger, Nature, 1937, 139, 925; Helv. Chim. Acta, 1937, 20, 1164); it lacks the characteristic inert hydroxyl group on  $\text{C}_{11}$ , but embodies the other features which appear to be essential for cortin activity, namely a double bond  $\alpha\beta$  with respect to the carbonyl group on  $\text{C}_3$  (since all the active compounds are inactivated on reduction) and the terminal hydroxyl group on  $\text{C}_{21}$  (since progesterone itself has no cortin activity). The compound was prepared from the acetate of  $\Delta^5$ -3-hydroxycholelic acid as follows:



The last compound is brominated to protect the double bond, oxidised and debrominated (*cf.* the preparation of progesterone, p. 273c), yielding the acetate of deoxycorticosterone. This synthesis is of great importance in view of the clinical uses of the compound. Deoxycorticosterone has recently been isolated in minute amount from the suprarenal gland (Reichstein and Von Euw, *ibid.* 1938, 21, 1197).

G. A. R. K.

**HORNBLLENDE.** An important rock-forming mineral belonging to the monoclinic series of the amphibole group, consisting mainly of metasilicates of calcium, magnesium and iron. The name hornblende is sometimes applied to the group itself, which includes the useful minerals asbestos (*q.v.*), nephrite and crocidolite (*q.v.*). More usually, however, it is restricted to the darker-coloured (green, brown, black) aluminous varieties, the composition of which is expressed by mixtures in various proportions of the molecules



etc. It forms part of many kinds of igneous rocks, *e.g.* hornblende-granite, syenite, basalt, etc., and crystalline schists, *e.g.* hornblende-schist.

L. J. S.

**HORNFELS** *v.* HORNSTONE.

**HORN LEAD:** Lead chloride,  $\text{PbCl}_2$ .

**HORN-QUICKSILVER.** *Calomel*,  $\text{Hg}_2\text{Cl}_2$ , occurs native in small quantities.

**HORN SILVER.** Native silver chloride *v.* CERARGYRITE.

**HORNSTONE** and **HORNFELS**, names applied to a variety of hard and tough, fine-grained and compact, splintery, siliceous rocks with a horny appearance, which have generally been formed by the baking action of igneous rock-masses on surrounding sedimentary rocks (sandstones, grits, shales, slates, etc.). They frequently show a banded structure representing the original bedding planes, but they do not break along these directions. The name hornstone is more usually applied by mineralogists to the highly siliceous kinds, and regarded as a variety of quartz allied to flint, chert, novaculite and jasper; whilst the German name hornfels is applied by petrographers to materials more of the nature of rocks, *e.g.* biotite-hornfels, andalusite-hornfels, tourmaline-hornfels, calc-silicate-hornfels, etc., the last-named having been produced by the thermal metamorphism of impure siliceous limestones. The Swedish *Hälle flinta* (meaning rock-flint) is also very similar in character; this may in some cases represent an altered felsitic lava, but in others it does not differ from hornfels. These materials are used as hones (*Whetstones*).

L. J. S.

**HORSE-CHESTNUT.** The horse-chestnut tree, *Æsculus hippocastanum*, is a native of Persia and Northern India, and is said to have been introduced into Europe in the sixteenth century. The nuts, closely resembling those of the sweet (edible) chestnut, are the "conkers" of school boys, but are injurious if eaten owing

to their content of toxic saponin and other bitter substances. When extracted with boiling water or preferably with dilute sodium carbonate solution the nuts leave a harmless residue of value as a cattle food (Sasaki and Kandatsu, *J. Agric. Chem. Soc. Japan*, 1936, 12, 875). According to Dechambre (*Compt. rend. Acad. Agric. France* 1917, 3, 927) the extracted nuts may be ground and used in breadmaking.

The bark of the tree contains the glucoside *æsculin* (*q.v.*) (6-β-glucosidoxy-7-hydroxycoumarin, Head and Robertson, *J.C.S.* 1930, 2435; Macbeth, *ibid.* 1931, 1288) with small proportions of the aglucone *æsculetin* (6:7-dihydroxycoumarin, Gattermann and Köbner, *Ber.* 1899, 32, 288). *Æsculin*, m.p. 200–202°, is extracted from the bark with boiling water, and the extract after treatment with lead acetate, and subsequently with hydrogen sulphide to remove excess lead, is concentrated until crystals are formed. *Æsculin* is hydrolysed by mineral acids or by the enzyme emulsin to glucose and *æsculetin*, m.p. 270°.

A second glucoside *fraxin* is also present in the bark. Hydrolysis of fraxin,  $\text{C}_{16}\text{H}_{18}\text{O}_{10}$ , yields glucose and *fraxetin*,  $\text{C}_9\text{H}_8\text{O}_6\text{OMe}$ , a methoxy-*æsculetin* (Koerner and Biginelli, *Gazzetta*, 1891, 21, ii, 452).

Horse-chestnut leaves contain quercitrin and the flowers contain quercetin.

Baker and Hulton (Analyst, 1917, 42, 353) give the composition of the hulled nuts as: water, 1.85–3.5; ash, 2.45–2.90; oil, 5.0–7.2; protein, 7.25–10.8; reducing sugars (as dextrose), 1.6–9.1; sucrose, 7.27–17.5; starch (Lintner), 21.9–47.8; starch (taka-diastase), 15.2–39.0; pentosans, 4.75–5.44; crude fibre, 2.0–2.6%. In an examination of the hulls Hilpert and Krüger (*Ber.* 1930, 72 [B], 400) give the following analytical data:

C, 54.5; H, 4.8; methoxyl, 2.2; lignin, 5.2; pentosans, 5.7%.

The nuts are of value in the manufacture of *n*-butyl alcohol and acetone by fermentation processes; yields of alcohol may reach 11–12% of the weight of the nuts (Henley, *J.S.C.I.* 1919, 38, 281r; Gill, *ibid.* p. 411r). Hirst and Young (*J.C.S.* 1939, 951) obtained yields of 10–20% of a starch having  $[\alpha]_D^{20} + 151^\circ$  and by means of the methyl derivative obtained three fractions of molecular weight 700,000, 650,000 and 430,000. The starch molecule probably corresponds with a chain length of 28 glucose units.

Belozerski and Dubrovskaja (*Biochimia*, 1936, 1, 665) isolated from the cotyledons of the nuts a globulin, *hippocastanin*, and a nucleoprotein. Hydrolysis of the latter yielded a protein having a nitrogen-distribution similar to that of hippocastanin and a nucleic acid yielding guanine, adenine, cytosine, thymine and lævulic acid but not uracil.

The use of the saponin of horse-chestnut as a substitute for white soap bark in certain therapeutic preparations is suggested by Roberg and Hoffmann (*Deut. Apoth.-Ztg.* 1939, 54, 416).

For an examination of the seed oil, *see* Masson (*Bull. Sci. pharmacol.* 1918, 25, 65).

A. G. Po.

**HORSE-FAT.** The fat obtained from the horse is of a yellowish colour and buttery consistency: as the rendering of horse-fat is not as a rule so carefully carried out as that of other edible animal fats, it is liable to be contaminated with remnants of tissues, to rancidify easily and to develop an unpleasant odour. On standing, it separates into a solid and a more unsaturated liquid portion, the latter being known as "horse oil" (not to be confused with horse's foot oil, *see below*). Both the fat and oil have weak drying properties and are, therefore, unsuitable for use as lubricants. In consequence of the increasing consumption of horse-meat, the fat has become a commercial article; it is used by the poorer classes on the Continent as a substitute for lard, and is no doubt used, upon occasion, as an adulterant of more expensive edible fats.

Low grade horse-fats are used in the manufacture of soaps and leather-greases. A process for protecting calcium carbide from the action of water vapour by a coating of oil from horse fat was patented by McRae (B.P. 25040/1905).

Horse-fat melts at about 34–39°C., and has an iodine value varying from 65 to 94 according to the part of animal from which it is derived: cf. Amthor and Zink, *Z. anal. Chem.* 1892, **31**, 381; Kalmann, *Chem.-Ztg.* 1892, **16**, 922; Gill and Rowe, *J. Amer. Chem. Soc.* 1902, **24**, 466; Dunlop, *Analyst*, 1907, **32**, 317 (the fat from the kidney-bed was found to have an iodine value of 110.6, the highest figure recorded for any horse-fat); Rosello, *Chim. et. Ind.*, 1929, Spec. No. (8e Congr. de Chim. ind., Strasbourg (1928) 520C. (examination of horse oils: the presence of palmito-dilinolin is reported).

The higher iodine value, and refractive index of horse-fat (51–59° Zeiss at 40°, i.e.  $n_D$  1.4600–1.4653) have been used in Germany as an official means of identifying horse-meat (cf. A. Beythien, "Laboratoriumsbuch f.d. Nahrungsmittelchemiker," 1931, 13. According to Pritzker and Jungkunz (*Z. Unters. Lebensm.* 1932, **63**, 30), however, the upper limit of 69° for the refractive index originally given by König ("Chem. d. menschl. Nahr.-u. Genussm.," 1910 (3) I, 420) and reproduced by Beythien and others is probably a misprint for 59°, a figure which is consistent with the iodine value and is also the one given in "Das Schweizerische Lebensmittelbuch," 1909 ed.).

Horse-fats contain about 24–33% of saturated acids, consisting of palmitic acid, with a small proportion (from 5–13%, on the whole fat) of stearic acid, oleic acid (50–55%) and linolic acid (about 10%) (v. Heiduschka and Steinruck, *J. pr. Chem.* 1921, [iii], 192, 241; Grossfeld, *Z. Unters. Lebensm.* 1931, **62**, 553; Pritzker and Jungkunz, *l.c.*). The presence of 1.7% of linolenic acid in horse-fat was reported by Heiduschka and Steinruck (v. Klimont, Meisl and Mayer, *Monatsh.* 1914, **35**, 1115) and rather more (about 4.5%) in the abdominal fat from the wild Western range horse (iodine value 82.7; Schuette, Garvin and Schwoegler, *J. Biol. Chem.* 1934, **107**, 635) which appears to be more unsaturated than the fat of the ordinary domestic horse.

The identification of horse-fat may be of importance in the examination of meat products

such as sausages, etc. According to Pritzker and Jungkunz, horse-fat may be differentiated from lard by the fractional precipitation method of Kreis and Roth (*Z. Unters. Lebensm.* 1913, **25**, 81), and fractional crystallisation of the acids from alcohol is suggested by G. Wolff (*Chim. et Ind.* 1934, Spec. No. (13e Congr. de Chim. ind., Lille, 1933), 8858): detection of it in admixture with lard or tallow is, however, a very much more difficult matter. It is stated to be detectable by biological methods depending upon the differentiation of albumins from different sources (cf. Wittels and Welwart, *Seifens.-Ztg.* 1910, **37**, 1014; Allen, "Commercial Organic Analysis," 5th ed., Vol. IX, p. 244; "Schweizerisches Lebensmittelbuch," 1917 ed.), but such methods would fail if all albuminous matter had been removed by refining. Paschke (*Z. Unters. Lebensm.* 1938, **76**, 476) relies upon the detection of linolenic acid in mixtures containing horse-fat, and has described a delicate modification of the hexabromide test for this purpose. The identification of horse-fat in lard by means of its characteristic absorption spectrum (max. at 310 m $\mu$ ) is claimed by Dorta and Reggiani (*Z. Unters. Lebensm.* 1939, **77**, 449).

*Horses' Crest-Fat* ("adepts colli equini") which is prized in Switzerland as a remedy for baldness and is obtained from the crest on the back of the neck, has been studied by Pritzker and Jungkunz (*Pharm. Acta Helv.* 1931, **6**, 201). Its refractive index (52.5–54.5° Zeiss at 40°, i.e.  $n_D$  1.4610–1.4623) and iodine value (75–84) are similar to those of horse-fat, but the content of unsaponifiable matter (0.13–0.19%) is distinctively lower than that of the body-fat (0.3–0.5%); the paler colour of the unsaponifiable matter derived from the crest-fat further serves to differentiate it from the body-fat. The body-fat gives orange-red colorations in the Bellier test, which is negative in the case of the crest-fat. Some 3–5% of paraffin wax or beeswax appears to be commonly added to the commercial crest-fat as a stiffener.

*Horse- (Bone-) Marrow Fat*, a non-drying fat of iodine value 77.5–80.5 (Zink, *Forschungsber. u. Lebensm.* 1896, **3**, 441), and *horse-bone fat*, iodine value 89.6 (v. Schenk, *Mitt. Lebensm. Hyg.* 1918, **9**, 215), are also obtainable from the horse.

*Horse's Foot Oil* is obtained from horses' feet by boiling them with water: samples examined by Lewkowitsch ("Chemical Technology of Oils, Fats and Waxes," 6th ed., Vol. 2, p. 495) and Amthor and Zink had iodine values of 74 and 90 respectively. As a rule the oil is not met with in commerce under its own name, as the feet are usually boiled out together with cattle feet and sheep's feet and the resulting oil is sold indiscriminately as "neat's foot oil," or as "animal oil."

E. L.

**HORSE-FLESH-ORE** (v. Vol. II, 32d).

**HORSE-RADISH.** The fleshy root of *Cochlearia armoracia* L., a cruciferous plant native to eastern Europe. The sliced or grated root is used as a condiment. Its characteristic flavour is largely due to the presence of propyl and isobutyl isothiocyanates. Recorded analyses show the root to contain (%):

Water . . . . .	73.8-76.7
Protein . . . . .	2.7-3.4
Fat . . . . .	0.3
N-free extract . . . . .	15.9-18.3
Fibre . . . . .	2.6-2.8
Ash . . . . .	1.5-1.6

More recently Friese (Z. Unters. Nahr.-u. Genussm. 1925, **49**, 194) gives the following data(%):

	Water.	Ash.
Whole root . . . . .	72.07	2.11
Inner layer . . . . .	76.96	1.79
Outer layer . . . . .	73.05	2.09

The percentage composition of the ash recorded by Friese (I) and by König (II) is as follows:—

	K <sub>2</sub> O.	Na <sub>2</sub> O	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
I. . . . .	30.34	11.66	9.27	2.67	0.09	0.21
II. . . . .	30.8	4.0	8.2	2.9	1.9	—

	Mn <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub>	Cl.
I. . . . .	0.09	7.54	27.09	9.37	0.84
II. . . . .	—	7.8	30.8	12.7	0.9

According to Noetzel (Pharm. Zentralk. 1935, **36**, 221) horse-radish "juice" contains 1.56-2.3% of dry matter, 0.3-0.5% of ash and 0.22-0.25% of mustard oil. The original roots (25-80% of water) contained 0.12-0.16% of mustard oil.

Peroxidase, present in horse-radish root, provided the basis of Buck's early studies of this enzyme. Elliot and Keihn (Proc. Roy. Soc. 1934, B, **114**, 210) record an examination of horse-radish peroxidase in relation to its hæmatin content. No relation was apparent between the proportion of hæmatin and the activity of the enzyme. All the hæmatin occurs free in the root as acid hæmatin.

Horse-radish is a good source of vitamin-C. According to Kedrov (Problems of Nutrition, U.S.S.R. 1934, **3**, No. 5, 20) 20 g. of root daily suffices to prevent scurvy in man if used as sole source of the vitamin.

A. G. Po.

#### HOWLITE (v. Vol. I, 586a).

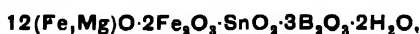
**HUCKLEBERRY.** The fruit of *Gaylussacia resinosa* Torr. and Gray, a native of the western hemisphere. In the central states of America the name is also given to the swamp blueberry, *Vaccinium corymbosum*. The fruit is eaten raw or cooked, and is frequently dried or canned.

The following percentage composition of the true huckleberry is recorded by Atwater and Bryant (U.S. Dept. Agric. Off. Exp. Sta. Bull. 1906, No. 28):

Water, 81.9; protein, 0.6; fat, 0.6; N-free extract, 16.6; fibre, 16.6; ash, 0.3%.

A. G. Po.

**HULSITE.** A black, opaque, orthorhombic (?) mineral originally described as a hydrous borate of ferrous and ferric iron and magnesium, but subsequently found to contain some tin (SnO<sub>2</sub>, 7.07% in a sample with a considerable amount of insoluble gangue), the formula being given as



It occurs as small crystals and tabular masses in a metamorphic limestone, near the contact of this rock with granite, at Brooks Mountain, Seward Peninsula, Alaska, and is associated with magnetite and tin-ore (A. Knopf and W. T. Schaller, Amer. J. Sci. 1908, [iv], **25**, 323; 1910, [iv], **29**, 543).

L. J. S.

**HUME-ROTHERY'S RULE.** In general, when one metal is alloyed with another, the first addition of a metal Y to a solvent metal X results in the formation of a homogeneous alloy with the same crystal structure as the parent metal X, and which may be called a *primary solid solution* of Y in X. These primary solid solutions are of two kinds, namely, *substitutional solid solutions* in which the solute atoms replace those of the solvent in its lattice, and *interstitial solid solutions* in which the solute atoms occupy the holes or interstices between those of the solvent. The extent of these primary solid solutions varies from complete miscibility of the two metals in the solid state (e.g. copper-nickel, silver-gold) to a solubility which is too small to be measured. When the concentration of solute atoms exceeds that of the limit of the primary solid solution, a new phase makes its appearance. In some systems (e.g. copper-silver) the new phase is a solid solution of X in Y, and in such cases the alloys, according to their compositions, fall into one of three types, a primary solid solution of Y in X, a primary solid solution of X in Y, and a mixture of the two primary solid solutions. In other systems intermediate phases are also formed, and these may be of fixed or variable composition. It is well known that, in the general case, the compositions of many of these intermediate phases are difficult to reconcile with the ordinary valencies of the elements, and it was first pointed out by Hume-Rothery<sup>1</sup> in 1926 that this is only to be expected when a truly metallic compound is formed. The valency compounds of ordinary chemistry are the result of the valency electrons being bound into stable groups (usually octets), and if metallic properties are regarded as resulting from the presence of free electrons, a metallic compound will not be expected to follow the usual valency relations. In searching for an alternative explanation of the compositions of the intermediate phases in alloy systems, Hume-Rothery was guided by the Electron Lattice Theory of Lindemann<sup>2</sup> which was attracting attention at the time. This theory has been discarded, but it led to the hypothesis that certain intermediate phases in alloy systems might be characterised by definite ratios of valency electrons to atoms, and this has been confirmed for a number of systems.

The first kind of alloy considered was that of the  $\alpha/\beta$  brass type, and Fig. 1 shows the equilibrium diagram of the system copper-zinc. Here the primary or  $\alpha$ -solid solution of zinc in copper is followed by a  $\beta$ -phase which has a body-centred cubic structure, in contrast with the face-centred cubic structure of copper itself. The composition of the  $\beta$ -phase is in the region of the equiatomic composition CuZn, although there is a wide range of solid solubility. The next phase, denoted  $\gamma$ , is in the region of 62 atomic per

cent. zinc, and has a characteristic crystal structure, and this in its turn is followed by the  $\epsilon$ -phase with a close-packed hexagonal structure, and a composition extending from about 78 to 87 atomic per cent. zinc, i.e. to the zinc-rich side of the composition 75 atomic per cent. zinc which would correspond with the formula  $\text{CuZn}_3$ .

Fig. 2 shows the equilibrium diagram of the system copper-aluminium, and this clearly has a general resemblance to that of the system copper-zinc. The  $\beta$ -phase in the system copper-

aluminium has a body-centred cubic structure, and its composition is in the region of  $\text{Cu}_3\text{Al}$ . The equilibrium diagram of the system copper-tin has some of the same characteristics, and here the composition of the  $\beta$ -phase is in the region of  $\text{Cu}_5\text{Sn}$ . It was pointed out by Hume-Rothery that, if the elements were given their normal valencies Cu 1, Zn 2, Al 3 and Sn 4, the compositions  $\text{CuZn}$ ,  $\text{Cu}_3\text{Al}$  and  $\text{Cu}_5\text{Sn}$  all corresponded with a ratio of 3 valency electrons to 2 atoms. Other examples were quoted, and

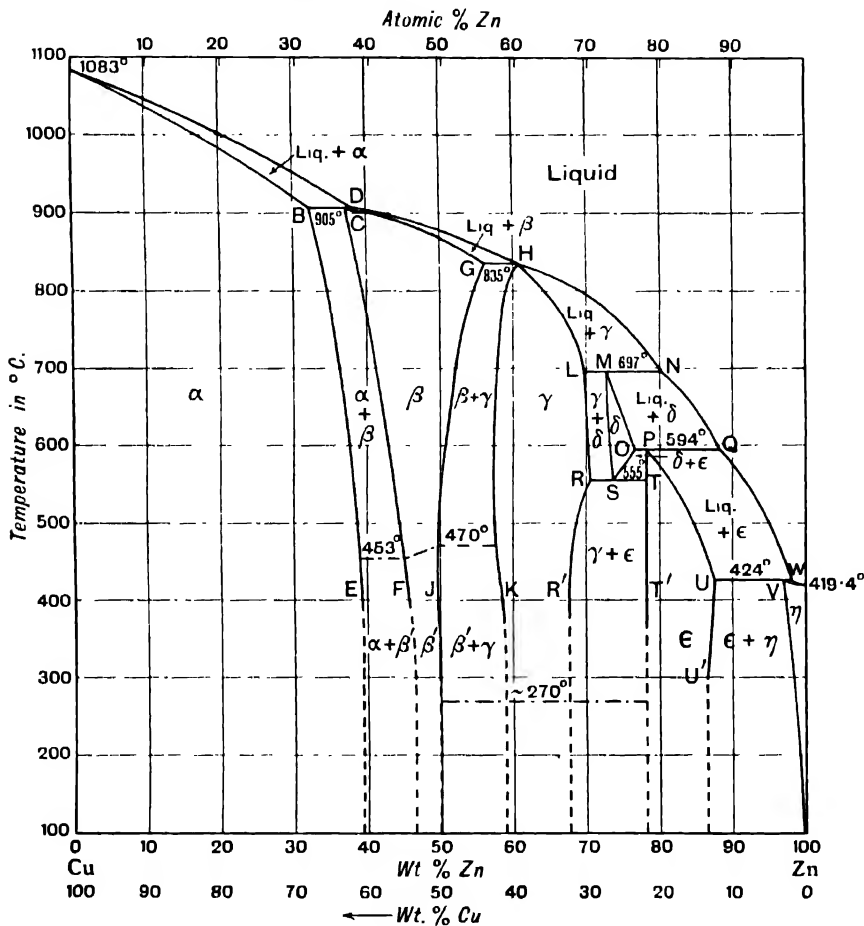


FIG. 1.

the idea was taken up by Westgren and his collaborators.<sup>3</sup> As a result of this and later work it was shown that in a number of alloys of copper, silver and gold with the elements of the B-subgroups, and with Be, Mg, Al and Si there was a general tendency for body-centred cubic structures to occur at a valency electron/atom ratio of  $3/2$ , whilst  $\gamma$ -brass structures were found at an electron/atom ratio of  $21/13$ , and close-packed hexagonal structures at an electron/atom ratio of  $7/4$ . These phases may conveniently be called electron compounds. The

work of Bradley and Gregory<sup>4</sup> showed that ternary electron compounds could be prepared, the type of crystal structure remaining the same when the proportions of the atoms were adjusted so that the electron concentration (i.e. the ratio of valency electrons to atoms) had the value characteristic of the structure concerned. This conception was carried further by the work of Ekman<sup>5</sup> and others, who showed that the same principle was followed in some alloys of the B-sub-group metals with elements of Group VIII, provided that the latter were assumed to possess



a zero valency. Thus in the system iron-zinc, a phase with the  $\gamma$ -brass structure was found to occur at a composition corresponding to the formula  $\text{Fe}_5\text{Zn}_{21}$ . Here, if the iron is assumed to possess zero valency, there are 42 valency electrons to 26 atoms, which gives the characteristic ratio 21:13 found in  $\text{Cu}_5\text{Zn}_{13}$  and  $\text{Cu}_5\text{Al}_4$ .

The above relations were discovered empirically, and clearly suggested that in this class of alloy the electron concentration was sometimes the predominant factor in determining the type of structure, although in other cases it was clear that the effect of electron concentra-

tion was outweighed by other factors. Of these the most important factor is the relative size of the different atoms, and, speaking generally, electron compounds are only formed in cases where the atomic diameters of the two elements do not differ too widely, the limiting difference being of the order of 25%. In cases where the two metals differ widely in electrochemical properties there is a tendency for electron compounds to disappear, and to be replaced by compounds which begin to resemble those of a normal valency type.

In Fig. 1 it will be seen that the  $\alpha/\alpha+\beta$  and  $\alpha+\beta/\beta$  phase boundaries have a characteristic

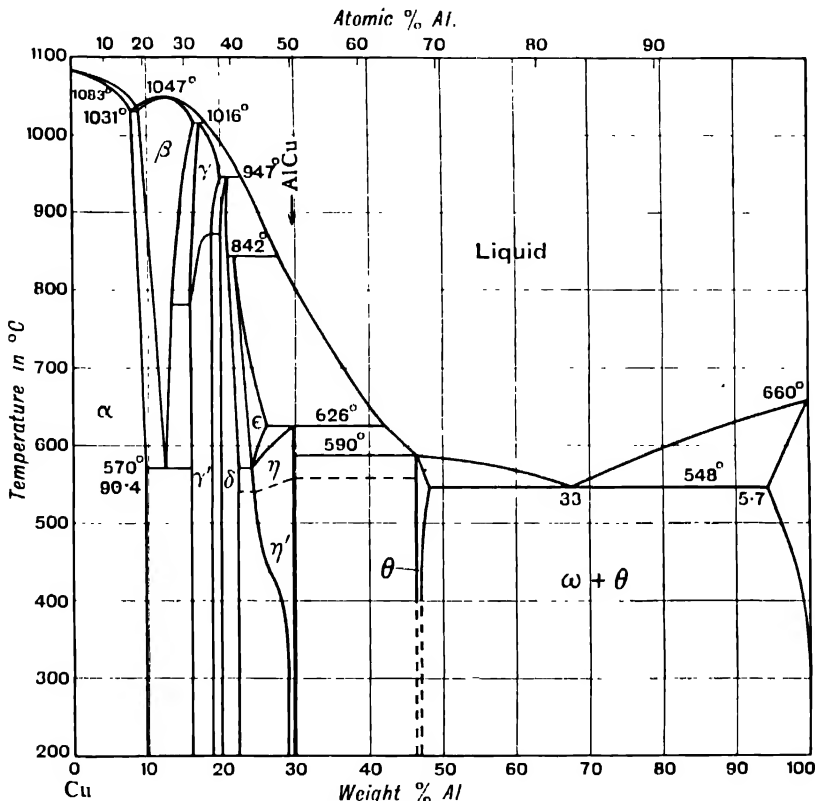


FIG. 2.

shape showing that the solubility of zinc in copper diminishes at high temperatures. It has been shown empirically by Hume-Rothery and collaborators<sup>6</sup> that this kind of phase boundary is controlled largely by the electron concentration, although the effects are modified by the relative sizes of the atoms in the alloy systems concerned, and these effects have been studied in detail by Hume-Rothery and Andrews.<sup>7</sup> From the empirical point of view, therefore, the position may be summarised by saying that in this class of alloy there are many cases in which both the type of structure and the form of the phase boundaries are determined largely

by the electron concentration, although this simple principle is often obscured by the effect of other factors such as the relative sizes or electrochemical characteristics of the atoms concerned.

These empirical relations received remarkable support from the theoretical work of Mott and Jones<sup>8</sup> on the modern electron theories of metals, especially as regards the theories of Brillouin zones (Brillouin, "Quantenstatistik," Berlin, 1931). Jones<sup>8</sup> was able to show that for the  $\gamma$ -brass structures the electron concentration was nearly that required to fill the first Brillouin zone. Although in other cases the

explanation was more complicated, the electron theory clearly supported the view that electron concentration was sometimes the predominant factor in determining the type of crystal structure or the form of phase boundaries, and Jones even developed a theory of the  $\alpha/\beta$  brass equilibrium in reasonable agreement with the facts. The work of Jones suggests that whilst the electron concentration is often the important factor, there is no reason why this should correspond with simple whole number ratios of atoms. In the above description reference has been made to formulae such as  $\text{CuZn}$ ,  $\text{Cu}_3\text{Al}$ , etc., in order to illustrate the principle in a simple way, but it must not be imagined that these exact ratios have any particular significance, or that any definite molecular species exist with these compositions. The important fact is that in the different systems, phases of the same structure tend to occur at roughly the same electron concentration.

Recent work by Lipson<sup>10</sup> has extended the principle to defect lattices. These are structures in which variation in composition takes place not by a process of substitution of one atom for another, but by one kind of atom dropping out of the lattice. In such cases it has been shown that characteristic changes occur at compositions such that the number of electrons per unit cell remains constant, and this is in agreement with the expectations of the electron theory. In normal structures with no defects, a constant number of electrons per unit cell is equivalent to a constant number of electrons per atom, or a constant electron concentration, but in defect lattices the number of electrons per unit cell is the fundamental characteristic.

#### REFERENCES.

1. W. Hume-Rothery, *J. Inst. Metals*, 1926, **35**, 309; *see also* W. Hume-Rothery, "The Structure of Metals and Alloys," Institute of Metals Monograph and Report Series, No. 1, 1936.
2. F. A. Lindemann, *Phil. Mag.* 1915, [vi], **29**, 127; *see also* W. Hume-Rothery, "The Metallic State," Clarendon Press, 1931.
3. A. Westgren and G. Phragmén, *Metallwirts.* 1928, **7**, 700. References to most of the papers by Westgren and his collaborators are given by U. Dehlinger, "Gitteraufbau metallischer Systeme," in G. Masing, "Handbuch der Metallphysik," Leipzig, 1935. This book gives much information on the present subject.
4. A. J. Bradley and C. H. Gregory, *Proc. Manchester Phil. Soc.* 1927-28, **72**, 91.
5. W. Ekman, *Z. physikal. Chem.* 1931, **B**, **12**, 57.
6. W. Hume-Rothery, G. W. Mabbott, and K. M. Channel Evans, *Phil. Trans.* 1934, **A**, **233**, 1.
7. W. Hume-Rothery, *Phil. Mag.* 1936, [vii], **22**, 1013; K. W. Andrews and W. Hume-Rothery, *Proc. Roy. Soc.* 1941, **A**, **178**, 464.
8. N. F. Mott and H. Jones, "Theory of the Properties of Metals and Alloys," Oxford University Press, 1936. This book is an invaluable source of reference for work on electron theories of metals.

9. H. Jones, *Proc. Physical Soc.* 1937, **49**, 243.

10. H. Lipson and A. Taylor, *Proc. Roy. Soc.* 1939, **A**, **178**, 232.

W. H.-R.

**HUMIC ACID.** The term applied from time to time to various acidic constituents of the black, spongy, semi-colloidal matter (humus) present in soils, peat, etc., resulting from the chemical and microbiological decomposition of plant and animal residues. Typical samples of humic acid are prepared by extracting soil or peat with very dilute alkali (concentrated alkali causes decomposition) and precipitating the brownish-black humic acid with dilute mineral acids. Numerous systems of purification or further fractionation have been adopted by different investigators. An average analysis of humic acid is **C** 61.9, **H** 4.2, **N** 3.3, **O** 30.6%.

Much discussion has centred round the nitrogen content of humic acid. Artificial humic acids, closely resembling the natural product, may be prepared by heating sugars with mineral acids. This suggests that the humic acid does not contain nitrogen as an essential constituent. The nitrogen invariably present in natural preparations has been regarded as ammoniacal nitrogen in ammonium humate. Not all this nitrogen, however, can be removed by customary methods for decomposing ammonium salts.

Preparations still more closely resembling natural humic acid are obtained by heating sugars with amino-acids under conditions favouring the production of hydroxymethylfurfuraldehyde. The latter substance on exposure to air is shown to be polymerised in the course of some months to yield a black substance, possessing the general properties of humic acid.

Attempts to prepare artificial humic acid have been numerous, but although there is a general similarity in the nature of the synthetic products, it cannot be established that any individual substance has been isolated. Nor can it be proved that any of the synthetic preparations is identical with the natural substance. Moreover, humic acid preparations from soil or peat vary considerably in their composition and properties according to the process of isolation adopted, and have not yet afforded proof that natural humic acid exists as a chemical entity. Many modern workers favour the view that the numerous preparations of natural humic acid consist of varied mixtures of substances similar in character but not chemically identical. Indeed Waksman, "Humus," Baillière, Tindall and Cox, 1938, suggests that to avoid misconception the term "humic" acid should be abandoned altogether.

A. G. Po.

**HUMIDITY AND HUMIDITY CONTROL.** *Introduction.*—Humidity is a general term applicable to the water vapour content of any gas. It is rarely used for gases other than air, and this restricted meaning is used throughout this article, but the application of the statements to other gases will be obvious.

There are three general methods of stating the humidity of air. The most fundamental is the *absolute humidity* which is the mass of water per unit volume of air, and is usually expressed

in terms of grams per cubic metre or grains per cubic foot. The absolute humidity at any temperature can be increased by adding water until the air becomes saturated, at which point it is in equilibrium with liquid water at the same temperature. (It is true that in the absence of nuclei such as dust particles or ions a super-saturated state may be obtained, but this is an unstable condition.) Humidity may also be quantitatively stated as the *vapour pressure* of water present in the air, but this is the least used of any methods of defining humidity, probably owing to the difficulty of measuring water vapour pressure in air by any simple direct method. Since water vapour obeys Boyle's law with considerable accuracy, the vapour pressure is proportional to the absolute humidity.

A much more useful measure is the *relative humidity* or *percentage saturation*, which is defined as the active absolute humidity expressed as a percentage of the maximum or saturation humidity at the same temperature. An alternative definition based on vapour pressures can be used and the difference between the two results is negligible in practice. Relative humidity is much more important than absolute humidity because it is closely related to the equilibrium moisture content of hygroscopic substances regardless of temperature changes, and has very direct application to such practical problems as drying. It should be noted that since the saturation absolute humidity and the vapour pressure of water increase with temperature, the relative humidity of a given quantity of air can be lowered by heating and raised by cooling, although no water is added or taken from the air.

Although humidity may be stated in these three ways it is always possible to relate one to the other if the temperature is known. Tables of saturation absolute humidity and of vapour pressure at various temperatures are available and therefore all measurements of humidity can be expressed in the way most convenient to the purpose in hand.

**Measurement of Humidity.**—*Absorption Method.*—The most fundamental method of measuring humidity is by absorption. A known volume of air is drawn over substances which completely remove the water (e.g. phosphorus pentoxide or silica gel). The mass of water absorbed can then be determined by weighing. This method is, however, cumbersome and slow and is little used in practice except for basic calibration purposes.

**Wet and Dry Bulb Hygrometers.**—The most usual method is to make use of the wet and dry bulb hygrometer, which consists of two mercury-in-glass thermometers, one of which has its bulb covered with muslin provided with a wick dipping into a water reservoir in order to keep it wet. Water then evaporates off the muslin at a rate depending on the relative humidity of the air, and the absorption of latent heat causes this thermometer to indicate a lower temperature (the wet bulb temperature) than the other which gives the dry bulb temperature. The difference of the readings is known as the bulb difference and from this the relative humidity is determined by reference to tables.

It is essential that the muslin and wick should be clean and be renewed frequently, and that the water should be pure. It is possible to use a wet and dry bulb instrument when the covering of the wet bulb is frozen but care must be taken when the film of ice is thin. Detailed instructions for such measurement will be found in the "Observer's Handbook" issued by the Meteorological Office in Great Britain, or similar publications in other countries.

The tables generally used in Great Britain for this type of hygrometer are "Hygrometrical Tables adapted to the use of the Dry- and Wet-Bulb Thermometer," by James Glaisher (4th ed., Taylor and Francis, London, 1866). To avoid the trouble of using tables, nomograms and various humidity-calculating devices have been produced and these are often a help in reducing observations to terms of relative humidity. The Meteorological Office issues a set of tables (M.O. 265) for use with wet and dry bulb thermometers exposed in Stevenson screens out of doors and these are intended for use in "light airs," whereas Glaisher's tables refer to the thermometers in still air. If still air were realised in practice, the sample of air which the hygrometer measured might not be the same as the rest of the space in which the observer was interested. If moving air be used it is found by experiment that for the same relative humidity the bulb difference increases with the velocity, but fortunately above a speed of 3 metres per sec. this increase is negligible. This fact forms the basis of two of the best types of wet and dry bulb hygrometer.

In the *slung or whirling psychrometer* two thermometers are fastened to a frame provided with a handle which enables them to be rotated, thus causing a stream of air to flow over the bulbs. This instrument is adopted as the standard for the measuring of humidity by the U.S. Weather Bureau, and detailed instructions for its use will be found in "Psychrometric Tables," published by the U.S. Government Printing Office, Washington. Briefly, these may be stated as follows: The bulb of one thermometer is covered with a wick and moistened, and the instrument whirled rapidly for 15–20 seconds, stopped and quickly read, the wet bulb having attention first. The whirling and reading are repeated until the wet bulb reaches its lowest temperature. While whirling the psychrometer the observer should walk to and fro thus obtaining a better average reading.

The other hygrometer employing moving air is called the *Assmann psychrometer* and is regarded as the best instrument of this type for standardisation purposes. A constant current of air is drawn by a fan driven by clockwork or by an electric motor over the bulbs of the two thermometers, one having the usual wet muslin cover. The bulbs are surrounded by highly polished metal shields so that the instrument is unaffected by radiant heat. The tables for use with it are practically identical with those of the whirling instrument, but the best tables are "Aspirations Psychrometer Tafeln" issued by the Prussian Meteorological Institute. These tables originally covered the range to 40°C. (104°F.), but this range has been extended

by Awbery and Griffiths (Proc. Physical Soc. 1932, **44**, 132) up to 100°C (212°F.).

It is not necessary to use mercury-in-glass thermometers, and mercury-in-steel thermometers, electrical resistance thermometers, thermo-couples or even bi-metallic temperature indicators are used in cases where the extra cost can be justified. With the mercury-in-steel thermometers it is possible to obtain enough power for a direct reading of relative humidity by means of a linkage system connecting the two indicating mechanisms to a pointer (e.g., Bateson, J. Sci. Instr. 1932, **9**, 94). With these variations from the usual mercury-in-glass thermometers records can be obtained and these are often of great value in industrial applications of humidity.

*Hygroscopic Methods.*—Other methods of measuring humidity depend on the change of length of hygroscopic substances when in equilibrium with atmospheres of different relative humidities. The most commonly used substances are hair, gold-beaters' skin, animal or vegetable membranes or textile fibres. Temperature changes of normal magnitude have little effect on these materials, and when cleaned from grease they can therefore be used for indicating and recording instruments calibrated directly in relative humidity. Unfortunately, the accuracy of such instruments is not great owing to lag and to changes of reading after they have been subjected to high or low humidities. It has been shown (D.S.I.R. Food Investigation Special Report No. 8, 1933) that gold-beaters' skin has the smallest lag and that horsehair maintains its calibration better than other substances. In cases where extreme accuracy is not necessary such instruments are very useful as they can be read directly; but they should be checked at intervals against a standard hygrometer.

*Dew Point Method.*—When air is cooled the relative humidity increases until the air becomes saturated. At this point (the dew point) water will be deposited as dew and this forms the basis of an accurate method of measurement. In order to detect the formation of dew a highly polished silver thimble is used and arrangements are made for cooling it, for instance, by the evaporation of ether. The temperature of the surface when the dew forms is best determined by means of a thermo-couple attached to the thimble. This method is not suitable for general use but forms an excellent means of calibrating empirical hygrometers. Full details of refinements obtaining high accuracy will be found in D.S.I.R. Food Investigation Special Report No. 8, 1933.

*Other Methods.*—Many other ways of measuring humidity have been proposed from time to time but the only one which will be mentioned here is that based on the different thermal conductivities of humid and dry air. The method is therefore identical with ordinary methods of gas analysis by *katharometer* which were described originally by Shakespear and Daynes (Proc. Roy. Soc. 1920, **A**, **97**, 273). It is a very accurate way of determining small amounts of water vapour in gases. (For further details, see H. A. Daynes, "Gas Analysis by

Measurement of Thermal Conductivity," Cambridge University Press, 1933.)

**Control of Humidity.**—It will be clear from what has been said that the relative humidity in any enclosed space can be changed by heating or cooling the atmosphere, but there is usually a very severe limitation to what can be done in this direction and therefore control is effected by adding or taking water from the air. Air is saturated at room temperature when it contains about 1% water by weight. The weight of water, therefore, required to change the humidity by 10%, which is a normal amount, is only 0.15% of the weight of the air if there is no leakage of air or condensation of water. The amount of water needed is therefore in general small and in some cases very crude methods can be used.

*Humidification.*—To increase the humidity in a room it is often sufficient to sprinkle water on the floor with a watering can or to allow steam to blow into the air from jets. The latter method usually results, however, in the introduction of much heat and the humidity in some cases is lowered when the steam is turned on. A far better way of introducing water is by means of specially designed humidifiers which break up the water into very small drops in which condition it readily evaporates. The absorption of heat in this process is often a great help in increasing the relative humidity in factories where machinery is giving off heat. The water may either be sprayed into the air, being atomised by compressed air, or the spraying may occur in an enclosure, through which air flows, and in its passage is consequently humidified and washed. A third type combines the function of a humidifier and ventilating plant, since air is humidified at some central point and distributed to various parts of the room or building by a trunking system. The relative advantages of these three types of plant depend greatly on the local conditions and cannot be discussed in detail here.

*Dehumidification.*—Interest in humidities lower than those normally occurring is generally the reason for installing a drying process. If it is allowable to heat the air this is clearly the easiest way of obtaining the necessary low humidity and is the general practice in drying methods. If heating is not allowable it is necessary to absorb the water from the air. When relatively small volumes of air are to be handled, fused calcium chloride is a very useful substance as it is cheap and the solution produced when water is absorbed is easily carried away by a drain. It has been found very useful in dehumidifying small laboratories and testing rooms. Sulphuric acid has been considered for the same purpose but has usually been rejected because of corrosion difficulties.

It is often preferred to use an adsorbent substance which can be regenerated. Silica gel, which is the best known example of this type, is pure silica manufactured in such a way as to have a porous structure which makes it capable of adsorbing up to 40% of its own weight of water without appearing wet or increasing in volume. When saturated it is heated and the water is given off, allowing the substance to be used

repeatedly (v. Vol. I, p. 150b). In practice it is arranged that three or four units are available, one being in use while the others are being regenerated or cooled. The change-over between the units can be effected at definite intervals by automatic means if desirable. A full description of such plant by Lees will be found in *Engineering*, 1932, **134**, 458. Alumina has been put forward as an alternative to silica gel and is used in very much the same way (*Engineering*, 1941, **152**, 406).

**Air-Conditioning Plants.**—The plants which have been described above are designed to correct humidity by the direct addition or removal of water vapour, little regard being paid to temperature. The object of an air-conditioning plant is to deliver at every point in the region served air which has been washed free from dust, at the desired temperature and humidity and with the correct air movement. The basic principle of such plants is that air is saturated with water at such a temperature that when it is heated to room temperature it will have the correct relative humidity. This may be a process of humidification or dehumidification according to circumstances, and air may also be heated or cooled during the process. The air is saturated by passing it through a very dense spray of water in a large chamber. Baffle plates remove any water drops and the air then passes through a heating chamber to give it the correct temperature. After this a fan delivers it to the distribution system. Details of the construction of such plants will be found in Moyer and Fittz, "Air Conditioning," McGraw Hill Book Co., New York, 1938. The control of these plants may be effected in many ways. The simplest of them is to use two thermostats which control the temperature of the spray-water and of the air as it leaves the plant.

When air is saturated in the manner described it is brought to a temperature known as the "temperature of adiabatic saturation" which, as pointed out by Carrier (*Trans. Amer. Soc. Mech. Eng.* 1911, **33**, 1005), is the same as the wet bulb temperature obtained in a ventilated wet and dry bulb hygrometer. The connection between the two cannot be explained on a theoretical basis, but the agreement in most cases is so close that the adiabatic saturation temperature is often spoken of as the wet bulb temperature.

When very low humidities are required with an air-conditioning plant it is necessary to cool the spray-water by a refrigerating plant or by some method such as rapid evaporation in a vacuum.

**Automatic Humidity Controls.**—The best results with a humidifying or dehumidifying plant can only be obtained with automatic control. An instrument for this purpose is essentially a hygrometer, fitted with some device to start the plant when the humidity departs from the desired value. The commonest form of control or "hygrostat" makes use of the change of length of hairs, textile threads or gold-beaters' skin. This type usually behaves very well as it is not subjected to large changes of humidity if the plant is kept running continuously. Another type is based on the wet

and dry bulb hygrometer, which, if it works on a true humidity basis, is complicated because the readings of two thermometers have to be subtracted and then corrected for temperature. This can be avoided by using a wet and dry bulb thermostat, but a small error in either instrument may then cause a considerable error in humidity.

The transmission of the indication of the hygrometer to the plant being controlled can be carried out electrically or by compressed air. The electrical method of transmission appears to be the simplest, but chattering of contacts often causes trouble with relays and this problem has to be given special consideration. With the compressed air method the sensitive element opens and closes a small leak in a system which is supplied through a smaller orifice, and consequently the presence or absence of the leak causes a large change of pressure which is employed in operating diaphragm valves or dampers. Space does not allow mention to be made of the many ingenious applications of these principles under practical working conditions (see *Bibliography*).

#### Humidity Control in Experimental Work.

—In any research or testing work with hygroscopic substances it may be necessary to control the humidity under which the work is carried out. If all the necessary operations can be carried out in an air-tight box it is often very simple to control the humidity by means of a large tray of saturated salt solution in the enclosure. This has a definite vapour pressure and therefore at a given temperature a fixed relative humidity. Tables of values will be found in "International Critical Tables" (Vol. I, p. 67). Sodium chloride may be specially mentioned, since its solubility changes little with temperature and therefore over a range of temperature it gives a relative humidity of approximately 73–75%. Sulphuric acid and glycerin solutions have been used for a similar purpose, but as they absorb or lose water their strength is changed and therefore the humidity is not constant as in the case of saturated salt solutions. Tables relating to sulphuric acid were given by Wilson (*J. Ind. Eng. Chem.* 1921, **13**, 326).

Where it is impossible to work in a small enclosure it is necessary to humidify the whole of the room. As accurate humidity control can only be effected when the temperature is also controlled, it is advisable to choose a room the temperature of which can be maintained constant. It should therefore have few or no windows and if possible an air-lock at its entrance. The humidity can be lowered by fans drawing air through a tower containing calcium chloride and raised by passing it through a similar tower containing wet pumice or coke. The fans can be controlled by any suitable type of electrical humidity control operating through relays.

#### Industrial Importance of Humidity.

—In the application of scientific principles to industry, humidity is assuming an ever increasing importance. This is obvious in connection with all problems relating to drying processes but there is also a much wider scope. When industrial materials are reviewed it is found that

a very large proportion are hygroscopic in character. A close investigation of their working properties shows that weather often has profound effects even in a building where the temperature is maintained approximately constant. These effects are therefore due to the changes of humidity and it is often economically sound to change the humidity artificially to ensure the best working conditions.

The behaviour of hygroscopic materials is to a large extent bound up with the formation of electrostatic charges. At high humidities the rate of leakage of these charges is so great that they are not detectable, but at low humidities they may become so marked as to exert considerable forces on the material being worked. Thus, in the textile trades threads and fabrics under dry conditions are often distorted from their normal paths through machines and become attached to any neighbouring earthed conductor with a resultant breakdown of the working. Another effect of these electrostatic charges is that dust or other small particles are often thrown off into the air causing discomfort and contamination. This effect is enormously reduced by the increase of humidity. Further, electrification may become so serious in some cases that sparks occur and in the presence of inflammable fibres the risk of fire is very considerable. Humidification has been used to reduce such risks.

Low humidities are of great value in works producing cables, transformers and other electrical apparatus in which the insulation must be kept in a very dry state.

**Humidity and Human Comfort.**—While the full consideration of this subject is outside the scope of this article, it should be noted that humidity is a large factor in the comfort conditions of an atmosphere especially in hot climates, the other factors being temperature and air movement. In Great Britain this subject has not therefore received as much attention as in America. The plants for giving comfortable conditions in large buildings are usually of the air-conditioning type fitted with refrigerators. The design of these plants is based on the results of much research work and excellent results are obtained.

Various instruments have been designed for measurement of comfort conditions, the best known of which is the *katathermometer* designed by Sir Leonard Hill. This is essentially an alcohol thermometer with a large bulb. The time for the temperature to drop from 100°F. to 95°F. is measured. From this a "cooling power" is determined and this has been related by much experimental work to comfort conditions. Another instrument is the *eupatheoscope* which is a black-painted copper cylinder 22 in. high by 7½ in. in diameter heated to 75°F., the loss of heat from this being recorded and scaled in figures of "equivalent temperature." For a full description, see D.S.I.R. Building Research Board Technical Paper, 1932, No. 13 (H.M. Stationery Office).

**Bibliography.**—The subject matter of this article is treated in a much fuller way, especially from the practical and industrial standpoints, in M. C. Marsh, "Controlled Humidity in

Industry, C. Griffin, London, 1935. Air-conditioning plants have been largely used in America and there is now considerable literature on this subject: see A. M. Green, Jr., "Principles of Heating, Ventilating and Air Conditioning," Wiley, 1936; W. H. Severns, "Heating, Ventilating and Air Conditioning Fundamentals," Wiley, 1937; C. A. Fuller, "Air Conditioning," Pitman, 1938; R. E. Holmes, "Air Conditioning in Summer and Winter," McGraw Hill Book Co., 1938; J. A. Moyer and R. U. Fittz, "Air Conditioning," McGraw Hill Book Co., 1938; J. R. Allen and J. H. Walker, "Heating and Air Conditioning," McGraw Hill Book Co., 1939; W. H. Stangle, "An Air Conditioning Primer," McGraw Hill Book Co., 1940. Reference should also be made to the "Journal of the Institution of Heating and Ventilating Engineers," London, and the "Transactions of the American Association of Heating and Ventilating Engineers," New York, also to two American periodicals, "Heating, Piping and Air Conditioning" and "The Aerologist."

M. C. M.

**HUMULENE** (v. Vol. II, 92a, 408d).

**HUMULON** (v. Vol. II, 92a).

**HUNGARIAN TURPENTINE** is the oleo-resin obtained from *Pinus pumilio* Haenke.

**HUTCHINSONITE.** Sulpharsenite of thallium, lead, silver and copper,



crystallised in the orthorhombic system, and one of the few minerals that contain thallium (18–25%) as an essential constituent. It is of rare occurrence as minute, red, transparent crystals in the white, crystalline dolomite of the Binnenthal in Switzerland.

L. J. S.

**HYACINTH or JACINTH.** A name loosely applied to several kinds of gem-stones of a yellowish-red or red shade, but more usually to *zircon* (native zirconium silicate,  $ZrSiO_4$ ). Other stones of similar colour to which the name is sometimes applied include: ferruginous quartz from Santiago de Compostella in the north of Spain (Compostella hyacinth); hessonite (v. GARNET); brown iodoicase or vesuvianite from Vesuvius; yellowish-red spinel from Minas Novas, Brazil; topaz from Brazil; and reddish-brown corundum (Oriental hyacinth). The *ὑάκινθος* or *hyacinthus* of the ancients was, however, a blue or purple stone, probably corundum (sapphire), or perhaps amethyst.

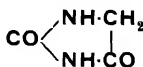
L. J. S.

**HYACINTH** (Artificial). Practically all hyacinth perfumes are based on two important synthetics, the natural perfume being rarely used. These two synthetics are  $\omega$ -bromostyrene,  $PhCH:CHBr$ , m.p. 7°, b.p. 220°,  $d$  1.4220,  $n_D$  1.6094; and phenylacetaldehyde,  $PhCH_2CHO$ , b.p. 205–207°,  $d$  1.050–1.085,  $n$  1.5265–1.5345. The latter important modern synthetic perfume is necessary in all the more delicate perfumes of the hyacinth and narcissus types, for which bromostyrene is rather coarse; but it is very apt to polymerise, and should be kept in dilute alcoholic solution.

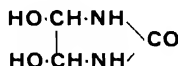
E. J. P.

**HYÆNIC ACID** ( $C_{26}H_{50}O_2$ ?) has been stated to occur as a glyceride in the secretion of the anal glandular pouches of the striped hyæna (Carius, *Annalen*, 1864, **129**, 168); the acid, which was stated to melt at 77–78°, probably consisted of a mixture of homologous fatty acids with an even number of carbon atoms.

E. L.

**HYALOPHANE** (v. Vol. I, 631b).**HYDANTOIN**, glycollylurea,

is found together with allantoin in the leaf buds of *Platanus orientalis* (Linn.) (Schulze and Barbieri, *Ber.* 1881, **14**, 1834); in beet juice (v. Lippmann, *ibid.* 1896, **29**, 2652); also in the pale sprouts growing from beets in moist warm weather (Pauly and Sauter, *ibid.* 1930, **63** [B], 2063). It is prepared (1) by reducing allantoin or alloxanic acid with concentrated hydriodic acid at 100° (Bayer, *Annalen*, 1864, **130**, 158); (2) by the action of excess of alcoholic ammonia on bromoacetylurea at 100° (Bayer, *Ber.* 1875, **8**, 612); (3) by the condensation of sodium dihydroxytartrate and urea in the presence of hydrochloric acid at 50–60° (Anschütz, *Annalen*, 1889, **254**, 258); (4) by the condensation of glyoxal and urea in the presence of hydrochloric acid (Siemonsen, *ibid.* 1904, **333**, 109); (5) from the compound:



(which is formed from formaldehyde and urea in water) by heating with hydrochloric acid (Pauly and Sauter, *l.c.*); (6) from amino acetonitrile by the action of potassium cyanate (Biltz and Slotta, *J. pr. Chem.* 1926, [ii], **113**, 233); (7) from ethyl hydantoate by heating at 135° for 7 hours or by warming with 25% hydrochloric acid (Harries and Weiss, *Ber.* 1900, **33**, 3418), or by heating with alcoholic ammonia at 100° (Harries, *Annalen*, 1908, **361**, 69); the ethyl hydantoate is prepared by the condensation of glycine ethyl ester hydrochloride with potassium cyanate (Harries and Weiss, *l.c.*) or by the interaction of glycine ester and sodium ethyl carbonate (Diels and Heintzel, *Ber.* 1905, **38**, 305). It may be prepared from hippuric acid by converting it into 1-benzoyl-2-thiohydantoin (formerly 3-benzoyl-) (Johnson and Nicolet, *J. Amer. Chem. Soc.* 1911, **13**, 1973) and then desulphurising this compound with an aqueous solution of chloroacetic acid (Johnson and Bengis, *ibid.* 1913, **35**, 1605). It is obtained from glycine by treatment with potassium cyanate and glacial acetic acid and evaporating the hydantoic acid so obtained to dryness with hydrochloric acid (West, *J. Biol. Chem.* 1918, **34**, 188; Wagner and Simons, *J. Chem. Education*, 1936, **13**, 265); and a yield of 90% is obtained by the condensation of glycine with nitrourea (Sah and Liu, *A.* 1937, 390).

Hydantoin crystallises in colourless needles, m.p. 216° (Schulze and Barbieri, Anschütz, *l.c.*)

Vol. VI.—19

217–220° (Harries and Weiss, *l.c.*); its heat of combustion at constant volume is +312.4 kg.-cal., and heat of formation +109 kg.-cal. (Matignon, *Ann. Chim.* 1893, [vi], **28**, 70). Its dissociation constant  $K_a$  is  $7.59 \times 10^{-10}$  (Wood, *Phil. Trans.* 1906, 1833); the dielectric co-

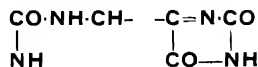
efficient  $\frac{d\epsilon}{dc} = 6.4$  ( $\epsilon$  = dielectric constant,  $c$  = concentration) (Devoto, *Gazzetta*, 1933, **63**, 50). For the absorption of light by hydantoin, see Asahina, *Bull. Chem. Soc. Japan*, 1929, **4**, 202. Irradiation with a quartz lamp causes opening of the ring since no ammonia is evolved but the amino-N (van Slyke) increases considerably (Lieben and Getreuer, *Biochem. Z.* 1933, **259**, 1). It is sparingly soluble in cold, readily in hot water, and the solution has a sweetish taste; it is soluble in 10 parts of boiling acetic acid.

Hydantoin is not attacked by ammonia, hydrochloric acid or dilute nitric acid; when boiled with baryta water it is converted into the barium salt of hydantoic acid, the heat of combustion of which is 308.9 kg.-cal. and heat of formation +181.6 kg.-cal. (Matignon, *l.c.*), m.p. 179–180°. Heating with ammonium sulphide at 150–155°

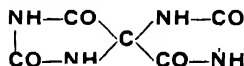
in a sealed tube or boiling for 120 hours with dilute ammonium sulphide gives glycine (Harries and Weiss, *Annalen*, 1903, **327**, 380; Boyd and Robson, *Biochem. J.* 1935, **29**, 542). The action of reductases from milk, blood, pancreas or liver extract causes cleavage with liberation of urea (Wada, *Proc. Imp. Acad. Tokyo*, 1934, **10**, 17). In its physiological action, hydantoin has a slight hyperglycæmic effect, counteracting to some extent the influence of maulin (Ishiki, *Folia Pharmacol. Japan*, 1932, **15**, No. 1, Breviaria 4).

Hydantoin forms *sodium* and *potassium salts* which are soluble in alcohol with difficulty and are hydrolysed by water (Bailey, *J. Amer. Chem. Soc.* 1906, **28**, 392). The *silver derivative*,  $C_3H_3O_2N_2Ag \cdot H_2O$ , is precipitated by silver nitrate from an ammoniacal solution of hydantoin (Weiss, *Annalen*, 1903, **327**, 375; cf. Bayer, *Annalen*, 1864, **130**, 160).

When equal weights of hydantoin and parabanic acid are heated at 150° for 1½ hours, 1:5 *dehydro-5:5'-dihydantyl*,



m.p. 178°, is formed; its sodium salt is yellow and crystallises from 20% sodium hydroxide with 4H<sub>2</sub>O, m.p. about 140°; reduction with hydriodic acid regenerates hydantoin (Biltz and Lachmann, *J. pr. Chem.* 1933, [ii], **136**, 217).

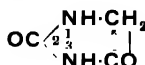
*Spiro-5:5'-dihydantoin*,

prepared by boiling 5-amino-4-hydroxy-4:5-dihydroic acid with concentrated hydrochloric acid, it crystallises in stout rhombohedra which slowly blacken and decompose above 400°. It is remarkably stable towards acids, and is not attacked by alkaline permanganate; it is converted by hot concentrated aqueous barium hydroxide into allantoin. It is the

parent substance of *hypocaffeine* (*trimethylspiro-5:5-dihydantoin*) (Biltz and Heyn, *Annalen*, 1916, 413, 38).

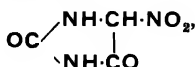
With 3:5-dinitrobenzoic acid in alkaline solution, hydantoin gives a purplish-rose colour (also given by many creatinine derivatives) which can be used for colorimetric determination (Benedict and Behre, *J. Biol. Chem.* 1936, 114, 515).

Substituted derivatives of hydantoin are referred to the ring,



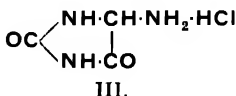
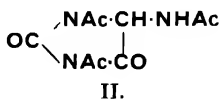
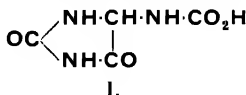
With regard to the isomerisation of hydantoin see Hahn and Seikel, *J. Amer. Chem. Soc.* 1936, 58, 647.

#### 5-Nitrohydantoin,



prepared by the action of nitric acid on hydantoin, forms shining crystals, melting and decomposing at 170° (Franchimont and Klobbie, *Rec trav. chim.* 1888, 7, 12; Harries and Weiss, *Annalen*, 1903, 327, 373).

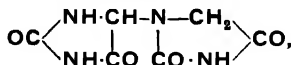
**5-Aminohydantoin hydrochloride**, 5-Carboxyaminohydantoin (*hydroxonic acid*) (I), obtained by the reduction of potassium allantoinate (Ponomarev, *Annalen*, 1870, 226, 228, 461; v. Vol. I, 239*d*) when boiled with acetic anhydride yields 1:3-diacetyl-5-acetylaminohydantoin (II) which is hydrolysed by boiling with a methyl alcoholic solution of HCl to give the hydrochloride of 5-aminohydantoin, m.p. 218–222° (III). The free base has not been isolated (Biltz and Giesler, *Ber.* 1913, 46, 3423; Biltz and Hanisch, *J. pr. Chem.* 1925, [ii], 111, 149):



**1:3-Diacetylhydantoin**, obtained by the action of acetic anhydride on hydantoin, has m.p. 104–105°, and yields 1-*acetylhydantoin*, m.p. 143–144°, when boiled with water, and this forms a sparingly soluble lead salt (Harries and Weiss, *Annalen*, 1903, 327, 355; Siemonsen, *ibid.* 1904, 333, 101).

**1:3-Dichlorohydantoin**, obtained in the form of lustrous crystalline leaves, m.p. 120–121°, by the action of chlorine on an aqueous solution of hydantoin, has the characteristic properties of a chloroimino compound (Harries and Weiss, *l.c.*; Siemonsen, *l.c.*; Biltz and

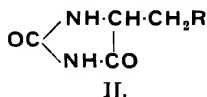
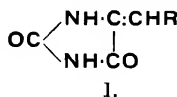
Behrens, *Ber.* 1910, 43, 1984). Attempts to prepare bromine derivatives of hydantoin have been unsuccessful; by the action of  $\frac{1}{2}$  mol. of bromine, hydantoin is converted into *isocallitric acid*,



m.p. 258–260°; when a larger proportion of bromine is employed, parabanic acid (oxalylurea) is formed, probably from an intermediate 5:5-dibromo-derivative.

**Condensation with Aldehydes.**—Hydantoin condenses with formaldehyde (1–3 mol.) in aqueous solution to form 1- (or 3-) *hydroxymethylhydantoin*, m.p. 125–135°; this yields *chloromethylhydantoin*,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\text{Cl}$ , m.p. 150–157°, when treated with phosphorus pentachloride or concentrated hydrochloric acid. When hydantoin is warmed with formaldehyde in the presence of acids, more complex products are obtained (Behrend and Niemeyer, *Annalen*, 1909, 365, 38).

Hydantoin condenses with aromatic aldehydes in the presence of glacial acetic acid and sodium acetate or in pyridine solution in the presence of piperidine or diethylamine, to form compounds of the type (I), which on reduction, e.g. with ammonium sulphide in aqueous or alcoholic solution or with hydrogen sulphide in pyridine, yield the corresponding 5-*aryl*-substituted hydantoin (II),

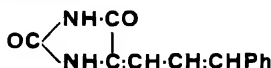


The following compounds have been described:

**5-Benzalhydantoin**, m.p. 220°; Johnson and Bates (*J. Amer. Chem. Soc.* 1915, 37, 383) record two isomeric modifications of benzalhydantoin: the ordinary form (*cis*), m.p. 220°, and a *trans*-form, m.p. 246°, which crystallises in aggregates of distorted needles (*cf.* Komatsu, *Mem. Coll. Sci. Eng. Kyoto*, 1912, 5, 13); for the absorption spectra of the two forms, see Hahn and Evans, *J. Amer. Chem. Soc.* 1928, 50, 806; and Asahina, *Bull. Chem. Soc. Japan*, 1930, 5, 354.

**5-Anisalhydantoin**, m.p. 243–244° (decomp.) yields a *bromo*-derivative, m.p. 247°; and on reduction with hydriodic acid forms 5-*p-hydroxybenzalhydantoin* (*tyrosine hydantoin*), m.p. 257–258°, from which tyrosine is obtained by prolonged boiling with hydriodic acid. The *tyrosinehydantoin*, m.p. 275–280°, described by Blendermann (*Bied. Zentr.* 1883, 209) is probably an optically active isomeride of this compound. **p-Hydroxybenzalhydantoin** has m.p. 315° (Boyd and Robson, *Biochem. J.* 1935, 29, 542); **piperonalhydantoin**, m.p. 245°. For the methyl ethers and acetoxy-derivatives of 3':4'-dihydroxybenzalhydantoin, see Deulofeu and Mendivelzua, *Z. physiol. Chem.* 1933, 219, 233.

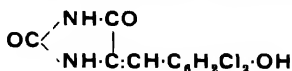
**5-Cinnamalhydantoin**,





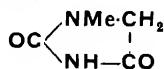
crystallises from hot glacial acetic acid in clusters of canary-yellow needles which melt at 272–273° to a red oil (decomp.) (Johnson and Wrenshall, J. Amer. Chem. Soc. 1915, **37**, 2133). 5-Fural-hydantoin has m.p. 232°; for the absorption spectrum, see Asahina, Bull. Chem. Soc. Japan, 1930, **5**, 354.

3:5'-Dichloro-4'-hydroxybenzylhydantoin,



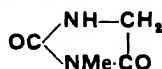
m.p. 300°. 5-p-Nitrobenzylhydantoin, m.p. 254° (Wheeler and Hoffman, Amer. Chem. J. 1911, **45**, 368). 5-o-Nitrobenzylhydantoin has m.p. 278–280°; nitration gives 1-nitro-5(o-nitrobenzal)-hydantoin, m.p. 224–226°; bromination in acetic acid gives the yellow 1-bromo-5(o-nitrobenzal)-hydantoin, m.p. 247–248°; while chlorination in acetic acid gives 1:3-dichloro-5(o-nitrobenzal)-hydantoin, m.p. 180–182° (decomp.) (Kozák and Musial, Bull. Acad. Polonaise, 1930, **A**, 432).

Alkyl and aryl substituted derivatives. 1-Methylhydantoin,



may be prepared (1) by fusing sarcosine and urea (Huppert, Ber. 1873, **6**, 1278; Horbaczewski, Monatsh. 1887, **8**, 586); (2) by passing cyanogen chloride through fused sarcosine (Traube, Ber. 1882, **15**, 2111); (3) by heating hydrocaffuric acid with baryta water (Fischer, Annalen, 1882, **215**, 286); (4) by reducing 3-methylallantoin with hydriodic acid (Fischer and Ach, Ber. 1899, **32**, 2748); (5) from methylhydantoic acid by long heating at 100–120° (Baumann and Hoppe-Seyler, *ibid.* 1874, **7**, 37; Salkowski, *ibid.* p. 188); (6) from the urea obtained by the action of potassium cyanate on methylaminoacetone hydrochloride by treatment with hydrochloric acid (Biltz and Slotta, J. pr. Chem. 1926, [ii], **113**, 233). It forms easily soluble prisms, m.p. 156°, from aqueous alcohol but sublimes in leaflets; the silver derivative,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\text{Ag}$ , forms difficultly soluble leaflets which become brown at 100°. It is considerably oxidised when administered subcutaneously to dogs (Gaebler and Keltch, J. Biol. Chem. 1926, **70**, 763). When heated with methylparabanic acid, 1-methylhydantoin yields dimethyl-5:5'-bihydantylidene, m.p. 273° (Biltz and Lachmann, *l.c.*). 1-Ethylhydantoin, obtained by heating equimolecular quantities of ethylglycine and urea at 120–125° (Heintz, Annalen, 1865, **133**, 65) or from N-cyanomethyl-N-ethylurea (Biltz and Slotta, *l.c.*), crystallises from alcohol and ether in rhombic plates, m.p. 103–104°, sublimes and is very easily soluble in alcohol and water, less so in ether; with diazomethane it gives 1-ethyl-3-methylhydantoin, m.p. 93° (Siemonsen, Annalen, 1904, **333**, 113).

3-Methylhydantoin,

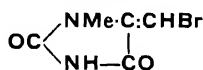


obtained by methylating hydantoin by means of methyl iodide, potassium hydroxide and methanol at 100° (Franchimont and Klobbie, Rec. trav. chim. 1889, **8**, 289; Siemonsen, *l.c.*), or with methyl sulphate (Biltz and Slotta, *l.c.*); from methylurea and glycine (Guareschi, Chem. Zentr. 1892, **I**, 140); or by heating  $\beta$ -methylallantoin with hydriodic acid on the water bath (Fischer and Ach, Ber. 1899, **32**, 2746); it crystallises in prisms, m.p. 182° and is very easily soluble in alcohol and boiling water, with difficulty in ether. The 1-nitro-derivative has m.p. 168° (Franchimont and Klobbie, *l.c.*) and the 1-acetyl-derivative forms needles, m.p. 134–135° (Siemonsen, *l.c.*).

3-Ethylhydantoin crystallises in leaflets from water, in prisms from alcohol, m.p. 103° (Bailey and Randolph, Ber. 1908, **41**, 2498; Harries and Weiss, Annalen, 1903, **327**, 378); nitration gives 1-nitro-3-ethylhydantoin.

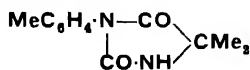
1:3-Dimethylhydantoin is formed by the action of diazomethane on 1-methylhydantoin; it has b.p. 174°/34 mm.

1:5-Dimethylhydantoin has m.p. 161–162° (Pinner, Ber. 1888, **21**, 2320) and yields 1-methyl-5-bromomethylenehydantoin,



m.p. 143–144°, by the action of bromine (Gabriel, Annalen, 1906, **348**, 50).

1-Phenylhydantoin from N-phenylglycine and urea or from chloracetylurea and aniline crystallises in needles, m.p. 191°; with potassium in alcohol it gives the potassium derivative,  $\text{C}_8\text{H}_7\text{O}_2\text{N}_2\text{K}$ , which decomposes at 370–378°, and is hydrolysed by water; bromination in acetic acid leads to substitution in the phenyl group (*p*-position) (Breustedt, J. pr. Chem. 1902, [ii], **66**, 254). 1-Phenyl-3-methylhydantoin melts at 185°; 1-phenyl-3-acetylhydantoin has m.p. 145–146° (Biltz and Slotta, *l.c.*). 1-p-Tolylhydantoin has m.p. 210° (Schwebel, Ber. 1877, **10**, 2045; **11**, 1128); 3-p-Tolylhydantoin, from *p*-tolylurea and glycine, has m.p. 206° (Quenda, Chem. Zentr. 1892, **I**, 140); 3-o-tolyl-5:5-dimethylhydantoin,



crystallises in thin prismatic plates, m.p. 172° (Bailey and McPherson, J. Biol. Chem. 1916, **11**, 2526; Ber. 1908, **41**, 2497). 1-Anisyl-3-methylhydantoin has m.p. 194°; 1-anisyl-3-acetylhydantoin, m.p. 172°.

Homologues of hydantoin containing one or two substituents in position 5 are most numerous and are prepared by the following general methods: (1) from the cyanhydrin of an aldehyde or ketone containing the group



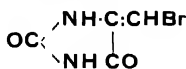
by the action of urea (Pinner, Ber. 1887, **20**, 2351; 1888, **21**, 2300; 1889, **22**, 685) or ammonium carbonate (Bucherer and Steiner, J. pr. Chem. 1934, [ii], **140**, 291; Wagner and Simons,

*l.c.*). Modifications of this method are due to Herbat and Johnson (J. Amer. Chem. Soc. 1932, **54**, 2463) who prepared the aminonitrile from the carbonyl compound by the action of hydrocyanic acid and ammonia, converted this to the ureidomitrile with potassium cyanate and then cyclised by warming with 20% hydrochloric acid. Berge (G.P. 566094) and also Slotta, Behnisch and Szyzka (Ber. 1934, **67** [B], 1529) heat the carbonyl compound with a cyanide and ammonium carbonate under pressure of carbon dioxide (2) By the action of dilute hydrochloric acid on the hydantoic acid obtained by evaporating to dryness a solution of an  $\alpha$ -amino-acid and potassium cyanate (Dakin, Amer. Chem. J. 1910, **44**, 48). This reaction is proposed for use in characterising and isolating amino-acids (Boyd, Biochem. J. 1933, **27**, 1838). Alternatively, the amino-acid may react with urea and baryta water (Lippich, Ber. 1908, **41**, 2953). (3) By reducing the compound obtained by the condensation of hydantoin with an aromatic aldehyde (Wheeler and Hoffmann, *l.c.*; Boyd and Robson, *l.c.*) and (4) from a substituted malondiamide by treatment with hypochlorite, the intermediate chloroamide

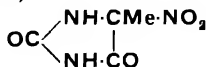
$\text{RR}'\text{C}(\text{CONH}_2)\text{CONHCl}$  (e.g.  $\text{R}=\text{R}'=\text{Et}$ ,

m.p. 135°) cyclising spontaneously in solution at room temperature (Rinkes, Rec. trav. chim. 1927, **46**, 268). 5-Substituted hydantoins can show optical activity and may be obtained in active forms by resolution with bases, e.g. brucine, or from optically active hydantoic acids or amino-acids by method (2) above (Sobotka, F.P. 736319; Sobotka, Holzman and Kahn, J. Amer. Chem. Soc. 1932, **54**, 4697).

5-Methylhydantoin (lactylurea), has m.p. 140° or 145° (Heintz, Annalen, 1873, **169**, 125; Urech, Ber. 1873, **6**, 1113) and on bromination yields 5-bromoethylenhydantoin,



m.p. 241–242° (Gabriel, Annalen, *l.c.*); 5-methyl-5-nitrohydantoin,



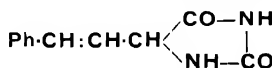
m.p. 148° (Franchimont and Klobbie, Rec. trav. chim. 1888, **7**, 13). 5-Ethylyhydantoin, m.p. 117–118°, yields 5-bromoethylenhydantoin, m.p. 230–236°, on bromination (Gabriel, *l.c.*); 5-propylyhydantoin has m.p. 136–5°; 5-isopropylyhydantoin, m.p. 146° (Berge, *l.c.*); 5-isobutylyhydantoin, m.p. 209–210° (Pinner and Lifschütz, Ber. 1887, **20**, 2351), 212° (Lippich, *ibid.* 1908, **41**, 2953); 1-5-isobutylyhydantoin, m.p. 212°,  $[\alpha]_D^{20} -68.2^\circ$  in normal sodium hydroxide solution, becoming zero in 30 hours owing to the ability of the ring carbonyl groups to enolise. 5-Phenylyhydantoin, m.p. 178°; the 5-acetyl-derivative has m.p. 145° (Pinner, *l.c.*); the 5-bromo-derivative melts above 200°, and is decomposed by hot water yielding 5-hydroxy-5-phenylyhydantoin (Gabriel, Annalen, 1906, **350**, 118). 1-3-Dimethyl-5-hydroxy-5-phenylyhydantoin has

m.p. 115–118° (Biltz and Bulow, *l.c.*). 3-Methyl-5-phenylyhydantoin has m.p. 161–162° (Pinner, Ber. 1888, **21**, 2320).

dl-5-Benzylhydantoin was prepared by Wheeler and Hoffman (Amer. Chem. J. 1911, **45**, 372) by heating benzalhydantoin with phosphorus and hydriodic acid. It crystallises from alcohol in lancet-shaped crystals or in prisms, m.p. 194–195°. Dakin and Dudley (J. Biol. Chem. 1914, **17**, 35) prepared *d*- and *l*-5-benzylhydantoins by hydrolysis of *l*- and *d*- $\beta$ -phenyl- $\alpha$ -ureidopropionic acids,



*d*-5-benzylhydantoin has m.p. 181–183° and  $[\alpha]_D^{20} +96.4^\circ$  in 50% alcohol; it racemises completely on standing in alkaline solution at room temperature; 1-5-benzylhydantoin has m.p. 181–183° on prolonged heating with concentrated acid it racemises completely. 5-p-Nitrobenzylhydantoin crystallises in pale yellow prisms, m.p. 238–240° (decomp.); 5-p-aminobenzylhydantoin has m.p. 145°; when diazotised and heated it yields tyrosinehydantoin (Johnson and Brautlecht, J. Biol. Chem. 1912, **12**, 187). 5-Anisylyhydantoin has m.p. 188–189°; 5-cinnamylhydantoin,

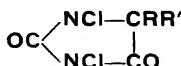


m.p. 171–172° (Pinner and Spilker, Ber. 1889, **22**, 685).

5:5-Dimethylhydantoin, formed from acetone cyanhydrin, has m.p. 175° (Urech, Annalen, 1872, **164**, 264; Errera, Gazzetta, 1896, **26**, i, 210), the 1-nitro derivative has m.p. 161–162°, the 1-acetyl derivative m.p. 192°; chlorination in cold aqueous solution gives 1:3-dichloro-5:5-dimethylhydantoin, while the action of diazomethane or methyl sulphate gives 3:5:5-trimethylhydantoin. 1:3:5:5-Tetramethylhydantoin obtained by methylation of the 1:5:5-compound, has m.p. 85°. dl-5-Methyl-5-ethylhydantoin has m.p. 149°; the optically active specimen prepared by Dakin (*l.c.*) had m.p. 172–173° and  $[\alpha]_D^{20} +32^\circ$ , this value remaining constant in alkaline solution. 5:5-Diethylhydantoin, m.p. 166°; 5:5-dipropylyhydantoin, m.p. 199° (Errera, *l.c.*; Biltz and Slotta, *l.c.*; Rinkes, *l.c.*). 5-Methyl-5-phenylyhydantoin has m.p. 197°; 5-ethyl-5-phenylyhydantoin (“nirvanol”) m.p. 197° and its sodium salt are hypnotics; it is tasteless but the sodium salt has a bitter taste (Werneck, Deut. med. Woch. 1916, **42**, 1193; Piotrowski, Chem. Zentr. 1916, **II**, 1182; from Münch. med. Woch. **63**, 1512; and Farbw. vorm. Meister, Lucius and Brüning, Swiss P. 72561); it has been resolved by means of brucine in absolute alcohol: *d*-5:5-ethylphenylyhydantoin, m.p. 237°,  $[\alpha]_D +123^\circ$  (in alcohol),  $+169^\circ$  (in alkali); the *l*-isomer has m.p. 235–237°,  $[\alpha]_D -121^\circ$  (alcohol),  $-167^\circ$  (alkali) (Sobotka, Holzman and Kahn, J. Amer. Chem. Soc. 1932, **54**, 4697). 5-Propyl-5-phenylyhydantoin, m.p. 170° (Farbw. vorm. Meister, Lucius and Brüning, Swiss P. 74189; 79190), 5-methyl-5- $\beta$ -phenylethylyhydantoin m.p. 180°, and 5-ethyl-5- $\beta$ -phenylethylyhydantoin also have hypnotic properties. For the preparation of other soporifics of this group, see

Chemische Fabrik von F. Heyden, G.P. 309508, 310426; Swiss P. 174461. 5-Methyl-5-benzylhydantoin has m.p. 226°; 5,5-dibenzylhydantoin m.p. 305° (decomp.); 5-phenyl-5-benzylhydantoin, m.p. 210° (Slotta, Behnisch and Szyzszka, l.c.).

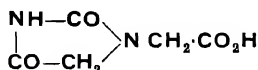
The action of sodium hypochlorite and free hypochlorous acid on 5,5-disubstituted hydantoins yields the 1:3-dichloro-derivative,



These compounds can be crystallised from chloroform, but are decomposed by water, alcohol or hydriodic acid regenerating the original hydantoin (Biltz and Behrens, Ber. 1910, 43, 1984).

1:3-Dichloro-5:5-diphenylhydantoin has m.p. 164° (decomp.) and yields 1:3-dimethyl-5:5-diphenylhydantoin when treated with methyl sulphate.

*Hydantoin-1-acetic acid*,



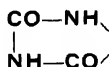
The ethyl ester condenses with anisaldehyde giving *ethyl 5-anisaldehydantoin-1-acetate* which crystallises with 1 mol. of alcohol, m.p. 215-216°. Digestion of the ester with sodium methoxide and methyl iodide yields *ethyl 3-methylhydantoin-1-acetate*, m.p. 91-92° (Reufrew and Johnson, J. Amer. Chem. Soc. 1929, 51, 1784). 5-Benzylhydantoin-1-acetic acid is a polypeptide hydantoin derived from phenylalanineglycine, has m.p. 184-185° and crystallises in flat prisms or rhombic plates (Johnson and Bates, *ibid.* 1916, 38, 1987).

*Hydantoin-3-acetic acid*, obtained by refluxing ureido-bismalonate ester



with 10% hydrochloric acid, has m.p. 196° (Cerechez, Bull. Soc. chim. 1931, [iv], 49, 52); *amide*, m.p. 225-226°; *anilide*, m.p. 215°; *methylamide*, m.p. 223°; *benzylamide*, m.p. 209-210°. A number of esters of hydantoin-3-acetic acid have been described: *methyl*, m.p. 91°; *propyl*, m.p. 116°; *butyl*, m.p. 95°; *sec-butyl*, m.p. 142°; *isobutyl*, m.p. 124°; *isoamyl*, m.p. 104°; *cyclohexyl*, m.p. 184°; *phenyl*, m.p. 205-206°; *benzyl*, m.p. 142°; *cholesteryl*, m.p. 304-305° (Loequeun and Cerechez, Compt. rend. 1929, 188, 177; Cerechez, Bull. Soc. chim. 1931, [iv], 49, 600, 602; Loequeun, Cerechez and Policard, *ibid.* 595; Policard, *ibid.* 607). Hydrolysis of hydantoin-3-acetic acid gives carbonylbisglycine (Wessely and Komm, Z. physiol. Chem. 1928, 174, 306).

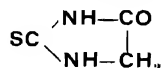
*Hydantoin-5-acetic acid*, m.p. 213-214°, is obtained together with its ureide,



m.p. 273-274°, by condensation of ethyl maleate

or fumarate with urea in the presence of sodium and alcohol at 75° (Jerzmanowska-Sienkiewiczowa, Roczn. Chem. 1935, 15, 202, 510; Amer. Chem. Abstr. 1936, 30, 2925). 5-Methylhydantoin-5-acetic acid has m.p. 214-215°. The ethyl ester, obtained by the method of Berge from acetoacetic ester, has m.p. 138° and gives an *amide*, m.p. 252° (decomp.) and *hydrazide*, m.p. 104-105°; hydrolysis with potassium hydroxide yields homoaspartic acid, m.p. 233° (decomp.) (Pfeiffer and Heinrich, J. pr. Chem. 1936, [ii], 146, 105). *Hydantoin-5-propionic acid* has m.p. 165°; *hydantoin-5-β-bromopropionic acid*, m.p. 228-230°; *Δ<sup>5</sup>-hydantoin-β-propionic acid*, m.p. 222-223°; *hydantoin-5-β-chloropropionic acid*, forms rectangular plates; *hydantoin-5-acrylic acid* m.p. 256-258° (Dakin, Biochem. J. 1919, 13, 398). For other derivatives of hydantoin see West, J. Biol. Chem. 1918, 34, 187.

**Thiohydantoins.**—2-Thiohydantoin,



was obtained by Klason (Chem.-Ztg. 1890, 14, Rep. 200). It may be obtained quantitatively by hydrolysis with hydrochloric acid of 2-thio-1-acetylhydantoin or of 2-thio-1-benzoylhydantoin (produced respectively by the action of potassium thiocyanate on glycine or on hippuric acid in the presence of acetic anhydride). Optically active derivatives may be obtained from optically active α-aminoacids by treatment with acetic anhydride and ammonium thiocyanate; if the thiocyanate is added after an interval, the thiohydantoin is racemised (Csönka and Nicolet, J. Biol. Chem. 1932, 99, 213). It crystallises in yellow prisms, m.p. 227-228° (decomp.). It is stable and yields stable sodium and potassium salts (Johnson and Nicolet, J. Amer. Chem. Soc. 1911, 33, 1973; 1913, 35, 780). 5-Methylthiohydantoin is a catalyst for the decomposition of sodium azide with iodine (Friedmann, J. pr. Chem. 1936, [iii], 146, 179). 2-Thio-3-p-tolylhydantoin, m.p. 228°, is converted into 3-p-tolylhydantoin on heating with an aqueous solution of chloroacetic acid (Johnson, Pfaw and Hodge, J. Amer. Chem. Soc. 1912, 34, 1045). 2-Thio-5-o-hydroxybenzylhydantoin, m.p. 107°, is readily desulphurised in the same way, yielding 5-o-hydroxybenzylhydantoin. 5:5-Dimethyl-3-o-tolyl-2-thiohydantoin, m.p. 195.5°, is prepared from o-tolyl mustard oil and potassium aminoisobutyrate (Bailey and McPherson, J. Amer. Chem. Soc. 1916, 38, 2525).

2-Thiohydantoin-5-propionic acid has m.p. 165° (Johnson and Guest, Amer. Chem. J. 1912, 47, 242).

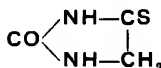
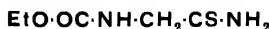
The benzal derivatives of thiohydantoin are dyes for wool, silk and cotton, giving yellow, orange and red tints. 5-Benzal-2-thiohydantoin, microscopic needles, m.p. 259° (Johnson and Nicolet, J. Amer. Chem. Soc. 1912, 34, 1048; cf. also Ruhemann and Stapleton, J.C.S. 1900, 77, 246); *acetyl* derivative, m.p. 260°. 5-Vanillal-2-thiohydantoin, m.p. 240°, *diacetyl* derivative, m.p. 261°; 5-cinnamal-2-thiohydantoin, m.p. 260°, *acetyl* derivative, m.p. 267°; 5-p-hydroxy-

*benzal-2-thiohydantoin*, m.p. 305° (Boyd and Robson, *Biochem. J.* 1935, **29**, 542; Namjoshi and Dutt, *J. Indian Chem. Soc.* 1931, **8**, 241; Johnson and Brautlecht, *J. Biol. Chem.* 1912, **12**, 184); 5-(3':4'-diacetoxybenzal)-2-thiohydantoin, m.p. 224–225°; 5-(3'-methoxy-4'-acetoxybenzal)-2-thiohydantoin, m.p. 246–247° (Deulofeu and Mendivelzua, *Z. physiol. Chem.* 1933, **219**, 233).

1-Acetyl-2-thiohydantoin crystallises from absolute alcohol in beautiful square tables; it melts at 175–176° to a clear oil without effervescence. 1-Acetyl-5-methyl-2-thiohydantoin prepared by the action of potassium thiocyanate on *D*-alanine, in the presence of acetic anhydride, crystallises in stout prisms, m.p. 161–162°,  $[\alpha]_D^{20} +118.5^\circ$  and the *dl*-form, m.p. 168–169° (Csonka and Nicolet, *l.c.*; Johnson and Nicolet, *J. Amer. Chem. Soc.* 1911, **33**, 1975; 1912, **34**, 1041; 1913, **35**, 1130; *Amer. Chem. J.* 1913, **49**, 200; *J. Biol. Chem.* 1912, **11**, 98).

2-Thiohydantoin reacts with aromatic aldehydes and acetic anhydride giving acetyl arylidene derivatives, the acetyl group being situated on the enolic form of the CO group (Namjoshi and Dutt, *l.c.*).

4-Thiohydantoin is formed by the condensation of carbethoxyaminothioacetamide in presence of alkali



It crystallises from hot water in spear-shaped twinned crystals and gradually decomposes above 200°; it hydrolyses with hydrochloric acid, yielding hydantoin and hydrogen sulphide (Johnson and Chernoff, *J. Amer. Chem. Soc.* 1912, **34**, 1208).

M. A. W.

**HYDNOCARPIC ACID** (v. Vol. II, 521b).

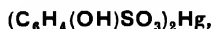
**HYDNOCARPUS OIL** (v. Vol. II, 521d).

"HYDRALDITE" (v. Vol. V, 320c).

"HYDRAMIN." Trade name for a combination of *p*-phenylenediamine and quinol. The same name has more recently been applied to a textile assistant (Krais, *Monatschr. Textil-Ind.* 1934, **49**, 138).

**HYDRARGILLITE** (v. Vol. V, 532a).

"HYDRARGYROL." Trade name for the mercury salt of phenol-*p*-sulphonic acid,



stated to be a useful non-corrosive antiseptic. "Asterol" is its more stable addition compound with ammonium tartrate.

**HYDRASTINE**,  $\text{C}_{21}\text{H}_{21}\text{O}_6\text{N}$ . An alkaloid occurring together with berberine and canadine in the root of "Golden Seal," *Hydrastis canadensis* Linn., to the extent of about 1.5%.

Its preparation and physical properties are described by Durand, *Amer. J. Pharm.* 1851, **23**, 112; Perrins, *Pharm. J.* 1861–1862, [ii], **3**, 546; Mahla, *Amer. J. Sci.* 1862, [ii], **36**, 57; Power, *Pharm. J.* 1884–1885, [iii], **15**, 297; Eijkman, *Rec. trav. chim.* 1886, **5**, 290; Freund

and Will, *Ber.* 1886, **19**, 2797; 1887, **20**, 88; Schmidt and Wilhelm, *Arch. Pharm.* 1888, **226**, 329; and Elsa Schmidt (*Amer. J. Pharm.* 1919, **91**, 270).

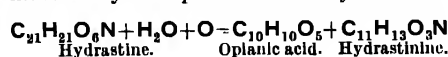
**Preparation.**—Hydrastine may be isolated from the sulphuric acid mother-liquor from which the berberine salt has crystallised (see BERBERINE). This is largely diluted with water, and almost neutralised with ammonia. On evaporation, ammonium sulphate, resin, etc., are filtered off, and the hydrastine precipitated from the cold filtrate by ammonia. The coloured precipitate is dissolved in alcohol (Perrins, Power), or ethyl acetate (Schmidt and Wilhelm), and the colouring matter removed by digestion with animal charcoal; the alkaloid crystallises from the concentrated solution. Purification of the hydrastine is effected by repeated crystallisation from alcohol.

Some authors prefer to extract hydrastine from the root before berberine, thus, according to Freund and Will, hydrastine is most readily obtained by percolating finely powdered hydrastis root with ether, and crystallising the ethereal residue from alcohol. Elsa Schmidt employs a similar method, using benzene as the solvent.

**Properties.**—Colourless, rhombic prisms, m.p. 132°. Insoluble in water, readily soluble in chloroform or benzene; less readily so in ether or alcohol;  $[\alpha]_D$  in chloroform,  $-67.8^\circ$  (Freund and Will); in chloroform,  $-63.8^\circ$ ; in dry alcohol,  $-49.8^\circ$ ; in 50% alcohol,  $+115^\circ$  (Carr and Reynolds, *J.C.S.* 1910, **97**, 1334). The ordinary salts of hydrastine are soluble in water, giving dextrorotatory solutions, but do not crystallise well (cf. Schmidt and Kerstein, *Arch. Pharm.* 1890, **228**, 49). Hydrastine and its hydrochloride, a hygroscopic powder, were official in the United States Pharmacopœia 1916, but have been dropped from the United States Pharmacopœia 1936; they are chiefly employed for the arrest of uterine hemorrhage in doses of  $\frac{1}{8}$  to  $\frac{1}{2}$  grain. Hydrastine is poisonous in larger doses.

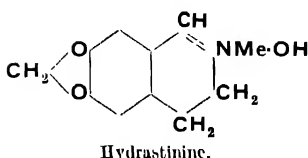
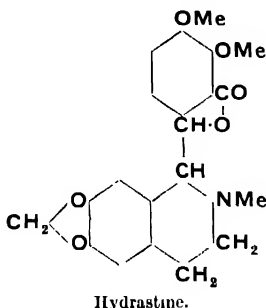
**Detection and estimation.**—The most characteristic colour reaction of hydrastine is the production of a fluorescent solution (due to the formation of hydrastinine) by the addition of permanganate to an aqueous solution of its sulphate (cf. Lyons, *Pharm. J.* 1885–86, [iii], **16**, 880). For other colour reactions of hydrastine, see Power, *ibid.* 1885–86, [iii], **16**, 1092; Labat, *Bull. Soc. chim.* 1909, [iv], **5**, 742, 745. The assay of hydrastis rhizome prescribed in the United States Pharmacopœia 1916 consists in the gravimetric estimation of the ether-soluble alkaloids, which should amount to not less than 2.5%. For other methods of assay, see Gordin and Prescott, *Arch. Pharm.* 1899, **237**, 439; 1901, **239**, 638; van der Haar, *Pharm. Weekblad.* 1911, **48**, 1302.

**Constitution.**—The oxidation of hydrastine by nitric acid yields opianic acid and hydrastinine.



The determination of its constitution is bound up with that of these fission-products

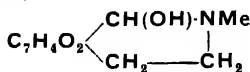
and is due mainly to the researches of Freund and Roser. The work, which has been reviewed by Freund (Annalen, 1892, 271, 311), leads to the following constitutional formula:



The complete synthesis of natural hydrastine has not been effected so far. Hope, Pyman, Remfry, and Robinson (J.C.S. 1931, 236) have described the synthesis of two optically inactive stereoisomerides of hydrastine but they have not yet been resolved. The mixture of nitrohydrastines obtained by the interaction of hydrastinine with nitromeconine was reduced to a mixture of two aminohydrastines. These were separated, and the amino-group was replaced by hydrogen by way of the hydrazino-hydrastines, yielding *dl-hydrastine-a*, m.p. 137°, and *dl-hydrastine-b*, m.p. 150–151°. The former was also obtained by the racemisation of natural *l*-hydrastine by means of aqueous alcohol under pressure (Marshall, Pyman and Robinson, J.C.S. 1934, 1315).

Hydrastinine,  $C_{11}H_{13}O_3N$ , is prepared by the oxidation of hydrastine (Freund and Will, Ber. 1887, 20, 88), and has been synthesised by Fritzsche (Annalen, 1895, 286, 18); Decker (G.P. 234850, 1910); Rosenmund (Ber. deut. pharm. Ges. 1919, 29, 200).

It may also be prepared from berberine (Freund, G.P. 241136, 1910), cotarnine (Pyman and Remfry, J.C.S. 1912, 101, 1595; see also Toptschiev, J. Appl. Chem. U.S.S.R., 1933, 6, 529) or safrrole (Kindler and Peschke, Arch. Pharm. 1932, 270, 353). Like berberine (*q.v.*), the free base occurs in two isomeric forms, in aqueous solution as the quaternary hydroxide shown above, and in the solid state as the carbinolamine,



(*cf.* Dobbie and Tinkler, J.C.S. 1904, 85, 1005).

It melts at 116–117°, crystallises from light petroleum, and is easily soluble in alcohol or ether, but sparingly so in water.

The hydrochloride, properly hydrastinium chloride,  $C_{11}H_{13}O_3NCl$ , like hydrastine and its hydrochloride, is not official in the United States Pharmacopoeia 1936. It melts and decomposes at 210°, and is easily soluble in water, giving a neutral solution showing a blue fluorescence. It gives no turbidity with ammonia, but sodium hydroxide causes a milky turbidity which disappears on shaking, and, on keeping, the solution deposits free hydrastinine.

Canadine,  $C_{20}H_{21}O_4N$ , occurs with crude hydrastine (*see above*), from which it may be isolated by fractional crystallisation of the nitrates, the canadine salt being less soluble. Silky needles, m.p. 132.5°,  $[\alpha]_D -298^\circ$  in chloroform (Schmidt, Arch. Pharm. 1894, [iii], 232, 136). On oxidation with iodine it is converted into berberine. By fractional crystallisation of tetrahydroberberine *d*-bromocampophosphonate, Gadamer (*ibid.* 1901, 239, 648) isolated a levorotatory base identical with canadine, which is therefore *l* tetrahydroberberine. Jowett and Pyman have found *l*-*α*-canadine methochloride in *Xanthorylum brachyacanthum* (J.C.S. 1913, 103, 293) (*cf.* Späth and Julian, Ber. 1931, 64 [B], 1311; Bersch and Seupert, *ibid.* 1937, 70 [B], 1121).

F. L. P.

**HYDRATION OF IONS.**—From the early days of the theory of electrolytic dissociation, it has been recognised that the ions of salts might be hydrated (or in general *solvated*) by attachment to solvent molecules, but it is only fairly recently that any quantitative results in this field have been obtained. With the hydrogen ion, the free proton  $H^+$  is linked with 1 mol. of water to form the hydroxonium ion  $H_3O^+$ , which is generally called the "hydrogen ion." In other solvents similar ions, *e.g.*  $(C_2H_5OH)H^+$  are probably formed. In some other cases also solvent molecules are thought to be attached by co-ordinate links to the solute ions.

Several methods have been used for the study of hydration of ions:

- (1) Absorption spectra.
- (2) Conductivity and viscosity measurements.
- (3) Distribution ratios and the solubility of gases in salt solutions.
- (4) Transport measurements.
- (5) Application of Stokes's law.
- (6) Energy changes in solvation of ions.

H. C. Jones in 1907–15 obtained evidence for the hydration of ions from absorption spectra of aqueous solutions of electrolytes. He found that certain salt solutions have a smaller capacity for absorbing radiation than pure water, and concluded that water was combined with solute ions, and that such water has a smaller capacity for absorbing radiation than free water.  $NH_4Cl$ ,  $NH_4NO_3$  and  $KCl$  solutions showed little difference from pure water in this respect. If a salt was dissolved in a mixture of two solvents, two absorption spectra were found, and on changing the composition of the solvent, the absorption spectra changed correspondingly in intensity, showing that the solvent molecules were in some way combined with

solute ions. If calcium chloride or aluminium chloride was added to a solution of cobalt chloride, the effect on the absorption spectrum was the same as if the solution had been concentrated. Hence it was assumed that the calcium chloride had taken some of the water molecules, and decreased the amount of "free" water for dissolving the cobalt chloride (Jones, *Z. Elektrochem.* 1914, 20, 552; Carnegie Inst. Pub., No. 60, 1907).

From his conductivity measurements Kohlrausch concluded that the ions were surrounded by atmospheres of water molecules, and that the electrolytic resistance was due to friction, which increased with the size of the ion atmosphere. In the case of highly hydrated ions the friction becomes almost the same as that between pure water molecules. Jones obtained further evidences of solvation from conductivity and viscosity measurements by working with mixed solvents, such as glycerin and water containing LiBr. The results were mainly qualitative.

Distribution experiments have been used as a means of determining the degree of hydration of ions (cf. J. C. Philip, *J.C.S.* 1907, 91, 711). The method depends on the assumption that if the ions are combined with water the amount of "free" water in the solution which is available for dissolving another substance, is reduced. The distribution of a substance between a non-aqueous solvent and a salt solution was studied, and assuming that the solubility in "free" water is the same as in pure water, the following results were obtained for molecular hydration:  $\text{Na}_2\text{SO}_4$ , 28.5;  $\text{HCl}$ , 4.4;  $\text{NaOH}$ , 20.5;  $\text{LiCl}$ , 8. Sugden (*ibid.* 1926, 174) used acetic acid distributed between amyl alcohol and salt solutions, and found that in many cases the degree of hydration is independent of temperature. H. A. Taylor (*J. Physical Chem.* 1925, 29, 995) determined the partition ratio of hydrogen chloride between benzene and salt solutions and came to the conclusion that aqueous solutions behaved like pure water, and that there was no difference between "free" and combined water. These measurements are primarily concerned with the activity of the solvent in various salt solutions and are not necessarily to be interpreted as a result of hydration.

A similar method used by Philip (*J.C.S.* 1907, 91, 711) depended on the difference between the solubility of a sparingly soluble gas in a salt solution and pure water. In some cases the absorption of the gas was found to be practically independent of the salt concentration, but where this was not so, hydration was assumed to have occurred, and the degree of hydration was calculated from the decrease in absorption.

Hüfner (*Z. physikal. Chem.* 1907, 57, 611) measured the decrease in solubility of nitrogen and hydrogen in solutions of organic substances, e.g. arabinose, and found that the decrease was proportional to the weight of substance in the solution. By this method Philip calculated the hydration of  $\text{KCl}$  as 8–11,  $\text{NaCl}$  as 14–16 and  $\text{BaCl}_2$  as 26–30.

When determining Hittorf transport numbers (this Vol., p. 237*d*) it is assumed that only the ions move and that the water is not transferred.

However, it was shown by Nernst in 1900 that the ions carry water with them, and that in concentrated solutions this effect is quite appreciable. He added an indifferent substance such as raffinose to the electrolyte solution and determined the concentration of the raffinose in the anolyte before and after electrolysis. If the electrolyte ions were unhydrated there would have been no change in the distribution of the raffinose throughout the solution, but a definite change round the anode was found. The results were not very conclusive, but with improved experimental technique later workers were able to calculate the relative hydration of the ions. Washburn (*J. Amer. Chem. Soc.* 1909, 31, 322), using a similar method to that of Nernst, determined the water so transferred, and calculated the true transport numbers  $n_c^T$  and  $n_a^T$  from the Hittorf values  $n_c^H$  and  $n_a^H$ . If  $\Delta N_w$  g.-mol. of water are transferred per faraday,  $F$ , to the cathode, and the solution contains  $N_s$  equivalents of solute to  $N_w$  equivalents of water, the solute corresponding to  $\Delta N_w$  of water is  $\frac{\Delta N_w N_s}{N_w}$ . Too little solute by this amount will be found in the cathode compartment.

$$n_c^T = n_c^H + \frac{\Delta N_w N_s}{N_w} \quad (1)$$

$$n_a^T = n_a^H - \frac{\Delta N_w N_s}{N_w} \quad (2)$$

In very dilute solutions  $n_c^T = n_c^H$ .

TABLE I.—TRUE AND APPARENT CATION TRANSPORT NUMBERS AT 25°C. IN 1.25*N* SOLUTION, AS DETERMINED BY WASHBURN.

	HCl	LiCl	NaCl	KCl	CsCl
$n_c^H$	0.820	0.278	0.366	0.482	0.485
$n_c^T$	0.844	0.304	0.383	0.495	0.491
$\Delta N_w$	0.24	2.5	0.76	0.60	0.53

Since  $\Delta N_w$  is the net transfer of water,

$$\Delta N_w = w_c n_c^T - w_a n_a^T \quad (3)$$

where  $w_a$  and  $w_c$  are the amounts of water carried by the anion and cation respectively.

Hence from (3)  $w_c = \frac{\Delta N_w}{n_c^T} + \frac{n_a^T w_a}{n_c^T}$ , and it is

possible to calculate the relative hydration of the ions. If it is assumed that the hydrogen ion has 1 mol. of water, then the numbers of molecules of water associated with other ions are  $\text{Li}^+=14$ ,  $\text{Na}^+=8.4$ ,  $\text{K}^+=5.4$ ,  $\text{Cs}^+=4.7$ .

Table I shows the remarkable fact that the cation transport numbers of the alkali metal chlorides increase with increase of atomic weight, whereas it would be expected that the mobility of the unsolvated ions would decrease with rise of atomic weight. Bredig in 1894 had suggested that the metal ions carried with them water which increased their size and thus slowed them

down, lithium carrying the most water and caesium the least, and this view is in accordance with the above results.

Remy (Z. physikal. Chem. 1925, 118, 161; Trans. Faraday Soc. 1927, 23, 381) measured the amount of water transported when the intermediate liquid was gelatinised, and in later work a parchment membrane was used. The change in volume of the liquids round the electrodes was measured by the rise of the meniscus in capillary tubes. Allowing for electro-endosmosis, and assuming that the parchment did not affect the movement of the ions, he calculated the following results for hydration. If it is assumed that one water molecule is associated with the hydrogen ion, the numbers associated with other ions are: K' 5, Na' 8, Li' 14, Cl' 4.

Baborovský (Z. physikal. Chem. 1927, 129, 129; 131, 129) carried out similar experiments but weighed and analysed the contents of the anode and cathode compartments. The results are as follows:—If one water molecule is associated with H', then the numbers associated with other ions are: Li' 14, Na' 8-9, K' 5, Cl' 4, Br' 2, I' 2 in normal solutions, but the hydration increases markedly in more dilute solutions.

The results of Washburn, Remy and Baborovský are in fair agreement, and those of Washburn were confirmed by Taylor and Sawyer (J.C.S. 1929, 2095) using urea as the reference substance.

Riesenfeld and Reinhold (Z. physikal. Chem. 1909, 66, 672) stated that the true transport number is independent of concentration, all such changes being due to hydration of ions.

If  $\frac{N_s}{N_w} = c$ , then  $n_c^T - n_c^H + c\Delta N_w$  from (1). If

$n_c^H$  is constant  $-\frac{1}{dc} \frac{d}{dc} \Delta N_w$  and the slope of the

graph made by plotting  $n_c^H$  against  $c$  is  $\Delta N_w$ . They combined this equation with the assumption that the water molecules form a shell round the ion, the volume of which can be calculated from Stokes's law, which states that

$u = \frac{F}{6\pi\eta r}$  where  $u$  is the velocity,  $r$  the radius of

the spherical ion,  $F$  the force moving it, and  $\eta$  the viscosity of the medium. If the volume of the ion is negligible compared with that of the water envelope, the volume of the latter can be found. If  $l_1, l_2$  are the mobilities of ions of

radii  $r_1, r_2$ , then  $\frac{r_1}{r_2} = \frac{l_2}{l_1}$ , and if  $A_1, A_2$  are the numbers of molecules of water attached to the

ions,  $\frac{A_1}{A_2} = \frac{l_2^3}{l_1^3}$ . In this way the following

values were found at infinite dilution, assuming that the hydrogen ion is unhydrated: OH' 11, K' 22, Cl' 21, Br' 20, I' 20, NO<sub>3</sub>' 25, Ag' 37, ClO<sub>3</sub>' 37,  $\frac{1}{2}$ Cd'' 55,  $\frac{1}{2}$ Cu'' 56, Na' 71, Li' 158. The values seem unreasonably large, and the modern theory of electrolytes indicates that the true transport number is not independent of concentration (Glasstone, "Electrochemistry of Solutions," Methuen, 1937, p. 166).

Remy (Z. physikal. Chem. 1915, 89, 529) assumed that certain large organic ions are

unhydrated, and from Kopp's atomic volumes calculated the supposed volume of the unhydrated hydrogen ion. By using Stokes's law, he found that the difference in radius between the hydrated and unhydrated ion was usually equal to the diameter of a water molecule. This calculation, however, involves rather uncertain ionic radii.

Ulich in 1926 took into account the volume of the ion and the compression of solvent molecules by electrostatic forces (electrostriction of the solvent).

All calculations based on Stokes's law give improbably high results, and it is very doubtful if the simple law holds for spheres of ionic dimensions.

A new approach has been opened by the study of energy changes in the solution of gaseous ions (i.e. unsolvated ions assumed to be in the gaseous state). W. M. Latimer (J. Amer. Chem. Soc. 1926, 48, 1234) calculated the energy of solution of gaseous ions in water, and obtained good agreement with the values which Born had found from a simple electrostatic expression for the energy change in bringing a charged sphere from a vacuum into a medium of dielectric constant  $D$ . Latimer found that the entropies of solution of gaseous ions vary linearly with the radii, and hence it is apparent that the energy effects on the solution of gaseous ions are determined by the size and charge of the ions. T. J. Webb (*ibid.* 1926, 48, 2589) calculated similarly the energy of solvation and the effect of electrostriction of the solvent. Fajans regarded the heat of solution of salts as due to two effects, (a) the energy required to dissociate the salt into free gaseous ions, and (b) the heat evolved when these are dissolved in water. Very high hydration values were obtained by this method of calculation, e.g. LiCl 187, NaCl 180.5.

More recently Bernal and Fowler (J. Chem. Physics, 1933, 1, 515) have derived expressions for the heat of hydration of ions, and their method is used as the basis of most of the recent work in this field.

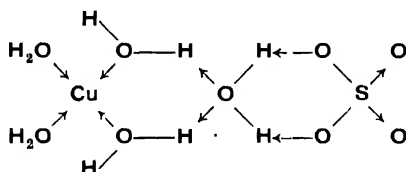
The values of the hydration of ions obtained by different methods show very poor agreement, and there is still no unanimity of opinion as to the exact relationship between the ions and solvent molecules.

Physical solvation doubtlessly explains many cases of hydration. This assumes that there is an increased concentration of water molecules in the immediate vicinity of an ion, and that the water molecules are held by electrostatic forces. Water is polar, and the molecular dipole orients itself so that in the case of a cation the negative or oxygen of the dipole is attracted to the ion. In the case of an anion, the hydrogen of the water molecule is attracted. There may be an induced dipole in the solvent molecule due to the field of the ion, and in the case of a small ion with a large charge, this induced dipole is large. Under the influence of an electromotive force the water molecules are dragged along with the ions. Born showed that the dipoles could be held so strongly by small ions that they would lose all degrees of freedom.

It is possible to obtain an expression for the electrical contribution to the heat of solvation of

ions, and if the force is purely electrostatic, this will be the total heat of solvation. The difference between the heats of solvation in two solvents should be equivalent to the heat of transfer of the ion from one solvent to another. The agreement between experimental results and those calculated on the assumption of physical solvation is not good. It is generally considered that when the sequence of ionic velocities is independent of the solvent, the solvation is physical.

Solvation can also be considered from the point of view of Werner's Co-ordination Theory. If one atom or group supplies both the electrons necessary to form a bond, the latter is known as a co-ordinate link, and the capacity of a group for co-ordination depends on its power of giving or accepting electrons. Six water molecules can co-ordinate with a metal ion to form a cation complex, and examples of such complexes are  $[\text{Co}(\text{H}_2\text{O})_6]^{1+}$  (the anion being  $2\text{Br}^-$ ,  $2\text{Cl}^-$ ,  $2\text{I}^-$ ) or  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2$  and similar compounds with Ni, Zn, Cd,  $\text{Fe}^{II}$ ,  $\text{Fe}^{III}$ , Ca and Al as nuclei. Copper sulphate pentahydrate has 4 mol. of water co-ordinated with the cation and 1 mol. co-ordinated with the anion as shown below:



It is seen that the anion and cation are bound together by co-ordination of an anion water molecule with two of the cation water molecules. Most cation water complexes are known to exist in solution, but anion complexes are in most cases only definitely known to be present in the solid state. Sidgwick, "Electronic Theory of Valency," Oxford University Press, 1927, has considered solvation from the electronic point of view, and has emphasised the importance of the donor and acceptor properties of hydroxylic solvents in forming co-ordinate links. This is shown by the structure of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in which it is seen that the oxygen atom of the OH group is capable of giving electrons, whilst the hydrogen atom can receive an electron. The solvation of ions increases the size of the ion and reduces the likelihood of ion association, since the ion centres have to be a certain minimum distance apart for association to take place. It was found that the ions of lithium salts undergo association in nitromethane, although the solvent has a large dipole moment which would induce physical solvation. It is thought that since nitromethane is a non-hydroxylic solvent, and can only coordinate with the cation, solvation is thereby reduced and ion association occurs. The velocity of the lithium ion is 3.36 times as fast in liquid ammonia as in water, whereas the silver ion is only 2.15 times as fast. It is probable that the silver ion tends to form a complex in ammonia, resulting in a reduction of the velocity, and that the lithium ion has a great affinity

for water and undergoes hydration in aqueous solution, which diminishes the velocity. This would explain the above observations on their relative velocities.

The general view now taken is that in a few cases chemical combination probably occurs between the ion and solvent molecules, and that other solvent molecules can be held by electrostatic forces. It is quite possible that in cases of physical solvation, a Grotthuss effect is produced in the electrolyte when the solute and solvent molecules have an atom or group in common. This implies a constant interchange of the common group or atom as the ion moves through the solution under the influence of an applied electromotive force.

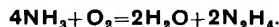
**Bibliography.**—H. S. Taylor, "Physical Chemistry," Macmillan, 1930, Vol. I, p. 686; Glasstone, "Electrochemistry of Solutions," Methuen, 1937, p. 45; Annual Reports of the Chemical Society, 1926, p. 27, and 1930, p. 351. J. R. P.

**HYDRATO-KANTEN- $\delta$  and  $\gamma$**  (r. Vol. I, 163a).

**HYDRATOPEKTIN** (v. Vol. V, 162a).

**HYDRAZINES.** The term "hydrazine" was first applied to the then unknown diamide,  $\text{NH}_2\text{NH}_2$ , by E. Fischer, but is commonly understood to include those derivatives in which the hydrogen atoms are replaced by other radicals. The reactions of such compounds divide them sharply into (a) those still containing an  $\text{NH}_2$  group and (b) those in which at least one of the hydrogen atoms of each amino group has been replaced. As all the compounds of any importance under (b) are hydrazo-compounds this account includes only those hydrazines containing the grouping  $\text{>N-NH}_2$  embracing hydrazine itself, mono- and unsym.-di-alkyl, -aryl, -acyl, and aralkyl hydrazines.

**Hydrazine,  $\text{N}_2\text{H}_4$ ,** was first obtained by Curtius (Ber. 1857, 20, 1632) in the forms of its hydrate and its salts by hydrolysing triazooacetic acid,  $(\text{CHN}_2\text{CO}_2\text{H})_3$ . The formation of hydrazine from many other organic compounds has also been reported, but it was a considerable time before simpler preparations from inorganic materials were elaborated. Thus traces of hydrazine are formed on exposing nitrogen and hydrogen to ultra-violet light, by passing a spark discharge through nitrogen-ammonia mixtures, by the direct oxidation of ammonia by cupric sulphate, by air alone (Raschig, Ber. 1907, 40, 4588), or in presence of noble metals (Krauss, Z. physikal. Chem. 1938, B, 39, 83):



Hydrazine is also formed in small amount by the reduction with sodium amalgam of nitric oxide-potassium sulphite,  $\text{K}_2\text{SO}_3 \cdot 2\text{NO}$  (Duden, Ber. 1894, 27, 3498) prepared by the interaction of nitric oxide and potassium sulphite (Divers and Haga, J.C.S. 1896, 69, 1610).

Hydrazine is most readily obtained, however, by oxidising ammonia with sodium hypochlorite (Raschig, l.c.; cf. Möller, Kong. dansk. Vidensk. Selsk. 1934, 12, No. 16) when chloramide initially

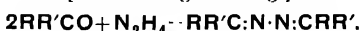


formed reacts with excess of ammonia. The yield is remarkably dependent on the presence of glue or gelatin (*see also* Joyner, J.C.S. 1923, 123, 1114), an effect which has been attributed to the influence of the colloid on the viscosity of the solution (dilution with a mobile solvent such as acetone exerts an unfavourable influence) or alternatively to the adsorbent properties of the colloid (the action of other strong adsorbents such as charcoal, colloidal silicic acid, etc., is in some measure comparable with that of glue). The base is conveniently isolated (preparation: Organic Syntheses, Coll. Vol. I, 1932, 302) as its sulphate,  $N_2H_4 \cdot H_2SO_4$ , distillation of which with aqueous alkali yields hydrazine hydrate,  $N_2H_4 \cdot H_2O$  (Curtius and Schultz, J. pr. Chem., 1890, [u], 42, 521), b.p. 119°. Its dehydration was achieved by de Bruyn (Rec. trav. chim. 1894, 13, 433; 1895, 14, 83; 1896, 15, 174; 1899, 18, 297) using barium oxide (barium and sodium hydroxides, calcium oxide and sodamide have since been used) and yields anhydrous hydrazine as a corrosive liquid, b.p. 113.5°, m.p. -1.4°, fuming strongly in air.

Pure hydrazine and its aqueous solutions are relatively stable but decompose rapidly in presence of alkali and air to nitrogen and water. With stronger oxidising agents, e.g. hypochlorites, reaction is very vigorous with rapid evolution of nitrogen.

Hydrazine is basic in character and although the pure compound reduces sulphuric and other oxygen-containing acids, a range of compounds containing tetra- and hexa-valent sulphur, etc., have been described. Hydrazine also forms metallic derivatives, thus excess of sodamide yields sodium hydrazine and an explosive zinc hydrazine has been described. Hydrazine is a good solvent for many inorganic salts some of which, however, suffer reduction.

Hydrazine condenses with carbonyl compounds to give azines which are often difficultly soluble compounds of high melting-point:



Hydrazine is used only to a minor extent in technical practice, e.g. as an antioxidant (U.S.P. 1973724) or in the application of azo-dyes (F.P. 766957) but is a valuable laboratory reagent as a reducing agent and for the precipitation of metals. Thus it affords a sensitive microchemical test for zinc (Ray and Sirkar, Mikrochem., Emich Festschr., 1930, 243) and may be used to separate aluminium and chromium (Maljarow, Chem. Zentr. 1930, II, 1408); iron from manganese (Jilek and Viovský, Coll. Czech. Chem. Comm. 1931, 3, 379); and to precipitate nickel, cobalt and cadmium in forms suitable for gravimetric estimation (Ray and Sirkar, J. Indian Chem. Soc. 1930, 7, 251).

Hydrazine may be detected by its ability to reduce gold salts (Curtius and Schrader, J. pr. Chem. 1894, [ii], 50, 318) or by the red acid-sensitive coloration given with ferric chloride after oxidising with alkaline ethyl nitrite to hydrazoic acid.

Semicarbazide,  $NH_2 \cdot CO \cdot NH \cdot NH_2$ , is prepared:

(1) By boiling hydrazine with (a) urea (Curtius and Heidenreich, Ber. 1894, 27, 56), or

(b) potassium cyanate (Biltz and Arnd, Annalen, 1905, 339, 250; cf. Bouveault and Loequin, Bull. Soc. chim. 1905, [iii], 33, 163).

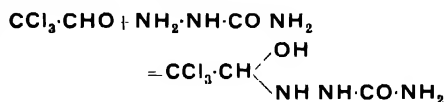
(2) From nitrourea by reduction either with zinc dust (Thiele and Heuser, Annalen, 1895, 288, 312) or electrolytically (Organic Syntheses, Coll. Vol. I, 1932, 472). The last method has the advantage of yielding the pure compound directly whilst in the older preparations it was necessary to convert it into a derivative (e.g. of acetone or benzaldehyde) from which the semicarbazide was regenerated.

Semicarbazide forms prisms, m.p. 96°, but is usually employed as its more stable salts with one equivalent of acid. It is used as reducing agent and both titrimetric (Maselli, Gazzetta, 1905, 35, i, 271) and gasometric (Datta, J. Amer. Chem. Soc. 1914, 36, 1014; 1916, 38, 2737) estimations depend upon this property.

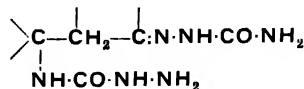
Semicarbazide readily reacts with carbonyl compounds to give characteristic semicarbazones:



This reaction is usually carried out by mixing cold or warm solutions of a semicarbazide salt (hydrochloride) and the carbonyl compound in water, with alcohol if necessary, and buffering excess acidity with sodium acetate when the derivative crystallises out. Occasionally, if the solution is subjected to long heating, the product contains hydrazine dicarbodiimide. The reaction is normal for most carbonyl compounds though abnormal reactions as with chloral are sometimes encountered:



(Khng, Compt. rend. 1909, 148, 569; Bull. Soc. chim. 1909, [iv], 5, 412), and  $\alpha$ -unsaturated carbonyl compounds often yield semicarbazide-semicarbazones of the type (Rupe and Hinterlach, Ber. 1907, 40, 4764):



Thiosemicarbazide,  $NH_2 \cdot NH \cdot CS \cdot NH_2$ , m.p. 181–183°, is prepared by boiling hydrazine hydrate with aqueous potassium carbonate and thiocyanate (Freund and Schander, Ber. 1896, 29, 2501). Thiosemicarbazones which are prepared similarly to the oxygenated compounds usually have low melting-points but are of value in that they give complex compounds with salts of heavy metals, particularly mercury (Neuberg and Neimann, *ibid.* 1902, 35, 2049; Jensen and Rancke-Madsen, Z. anorg. Chem. 1936, 227, 25). Thiosemicarbazide is a relatively non-toxic antioxidant suitable for spraying dried fruits to prevent discoloration (U.S.P. 2088458) and for stabilising adrenaline (U.S.P. 2047144). It exerts a specific influence on the quality of silver electroplating (Egeberg

and Promisel, *Trans. Electrochem. Soc.* 1938, **74**, Preprint 13) and acts as an anticorrosion assistant on iron or iron alloys (F.P. 652598).

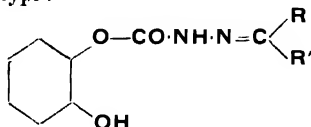
#### 4-Phenylsemicarbazide,



m.p. 122°, is formed on boiling semicarbazones with aniline and then hydrolysing and separating the ketonic constituent (Borsche, *Ber.* 1905, **38**, 832), but is best prepared by heating phenylurea with hydrazine hydrate (*Organic Syntheses*, Coll. Vol. I, 1932, 439). Phenylsemicarbazide is occasionally used as a ketone reagent (Braun and Steindorff, *Ber.* 1905, **38**, 3097; Sah and Ma, *J. Chinese Chem. Soc.* 1934, **2**, 32) giving derivatives which form complexes with heavy metals such as iron, cadmium, cobalt, etc. (Smith, *J.C.S.* 1937, 1354; Jensen and Ranche-Madsen, *Z. anorg. Chem.* 1936, **227**, 25); it has also been incorporated in therapeutic preparations (*Svensk Farm. Tidskr.* 1938, **42**, No. 15, Suppl. 1).

Benzhydrazide, *o*-, *m*- and *p*-nitrobenz- and other aryl hydrazides, obtained by heating the carboxylic amides or esters with hydrazine hydrate, give well-defined crystalline aldehydic or ketonic derivatives which are sometimes more conveniently handled than the phenyl hydrazones (Curtius *et al.*, *J. pr. Chem.* 1894, [ii], **50**, 275, 295; 1895, **51**, [iii], 165, 353). Like other hydrazides benzhydrazide undergoes chemiluminescent oxidation by hypochlorite (Courtot and Bernanose, *Compt. rend.* 1937, **205**, 989). Sah and his co-workers have prepared a large number of nitrobenzhydrazones (*Sci. Rep. Nat. Tsing Hua Univ. Ser. A*, 1934, **2**, 357; Chen, *J. Chinese Chem. Soc.* 1935, **3**, 251) some of which seem to be of distinct value, *e.g.* for the complete isolation of vitamin (Schorigin and Smoljaninova, *A.* 1935, 750; for microchemical use, *see* Griebel and Weiss, *Mikrochem.* 1927, **5**, 146). Aryl acid hydrazides are efficient oxidation-inhibitors (G.P. 504436).

Einhorn (*Annalen*, 1898, **300**, 135; 1901, **317**, 190) has shown that hydroxyacyl hydrazones of the type:



are formed particularly easily by aldehydes but much less readily by ketones and possess the property of dissolving in alkali and being precipitated unchanged by acid.

Semioxamamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , m.p. 220–221°, prepared by boiling hydrazine with oxamethane in alcohol, is recommended as a reagent for aldehydes, *e.g.* furfural and cinnamaldehyde (Kerp and Unger, *Ber.* 1897, **30**, 585).

Phenylhydrazine,  $\text{H}_2\text{N}\cdot\text{NHPh}$ , is conveniently prepared by reducing benzene diazonium salts with stannous chloride (Hantzsch, *ibid.* 1898, **31**, 346), zinc dust (Meyer and Lecco, *ibid.* 1883, **16**, 2976), alkali sulphite (Fischer, *ibid.* 1875, **8**, 590; *Annalen*, 1878, **190**, 73; *Organic Syntheses*, Coll. Vol. I, 1932, 432) or electrolytically (Fichter and Willi, *Helv. Chim.*

*Acta*, 1934, **17**, 1416). The manufacture by the reduction of nitrobenzene using lead oxides is the subject of patent claims (G.P. 486598) and it is also produced by the very remarkable action of fluoramine ( $\text{NH}_2\text{F}$ ) on aniline (F.P. 735020).

Phenylhydrazine has m.p. 19.6° (Fischer, *Ber.* 1908, **41**, 74), b.p. 243.5°/760 mm. (corr.),  $d_4^{25}$  1.0970 (Perkin, *J.C.S.* 1896, **69**, 1209). It is very susceptible to oxidation and the hydrochloride is usually used for the preparation of phenylhydrazones. It is weakly basic and forms mono-acid salts, although easily dissociable salts with two equivalents of inorganic acids have been described. The base and many of its derivatives are toxic.

Phenylhydrazine may be detected by its colour reactions with sodium hypobromite (Dehn and Scott, *J. Amer. Chem. Soc.* 1908, **30**, 1422), 2,4-dinitrobenzaldehyde (Sachs and Kemp, *Ber.* 1902, **35**, 1230) or formaldehyde and sodium nitroprusside (Simon, *Compt. rend.* 1898, **126**, 483; *Bull. Soc. chim.* 1898, [iii], **19**, 299). The oxalate crystallises well and provides a means of identification (Bamberger and Suzuki, *Ber.* 1912, **45**, 2752). More conclusive is its characterisation as a phenylhydrazone (*see* HYDRAZONES). It is estimated by its reducing action on Fehling's solution (Strachle, *Monatsh.* 1891, **12**, 525; *cf.* Maclean, *Biochem. J.* 1913, **7**, 611) or on arsenic acid (Causse, *Compt. rend.* 1897, **125**, 712; *Bull. Soc. chim.* 1898, [iii], **19**, 148).

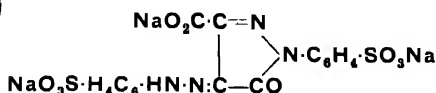
Phenylhydrazine is used in the laboratory to characterise carbonyl compounds as phenylhydrazones and sugars as osazones (mechanism: Kenner and Knight, *Ber.* 1936, **69** [B], 341) and as an analytical reagent, *e.g.* for molybdenum (*see* Schmidt, "Anwendung der Hydrazine in der analytischen Chemie," Stuttgart, 1907, p. 31), for aluminium in presence of iron (Ishimaru, *Sci. Rep. Tôhoku Imp. Univ.* 1936, **1**, 25, 780), for mercury (Miller, *Chem.-Analyst*, 1938, 27, 9). In technical practice phenylhydrazine is the source of pyrazolone medicinals ("antipyrene," "pyramidone"), bactericidal azo-compounds (Jug.P. 13777) and of some azo dyes such as Eriochrome Red (U.S.P. 1856413). Attempts have also been made to put some of its derivatives to therapeutic uses in the treatment of tuberculosis (review: Schnitzer, *Z. angew. Chem.* 1930, **43**, 744). Phenylhydrazine is an efficient antioxidant (B.P. 312774) and an effective softener for natural and synthetic rubber (B.P. 488701) particularly when protected by the presence of another antioxidant, and that it similarly improves cellulosic materials such as those intended for surgical use is claimed (Swiss P. 183210).

#### Phenylhydrazine-*p*-sulphonic acid,



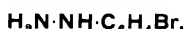
m.p. 280°, is prepared by sulphonating phenylhydrazine or reducing diazotised sulphanilic acid. Its reactions are often abnormal as when it forms addition compounds with aromatic aldehydes and ketones (*cf.* however, its use in isolating the corpus luteum hormone, Swiss P. 170618, and its reaction with sugars, B.P. 340619). It nevertheless yields pyrazolones

with aliphatic diketones, and the yellow dyestuff *tartrazine* with dihydroxytartaric acid,



(G.P. 34294; Swiss P. 119718); it is also the source of dipyrazolones (F.P. 44843) and nitro-colours (B.P. 409512). Phenylhydrazine-*p*-sulphonic acid has been applied in the form of long-chain hydrazones (e.g. of lauric aldehyde) as a textile assistant (F.P. 755143). Its possible therapeutic action on malignant tumours has been investigated (Boylard, *Biochem. J.* 1938, **32**, 1207).

#### *p*-Bromophenylhydrazine,



m.p. 105.5°, prepared by brominating a phenyl hydrazone and hydrolysing the product (Humphreys, Bloom and Evans, *J.C.S.* 1923, **123**, 1768) or directly by brominating phenylhydrazine and reducing the resulting bromodiazonium bromide (Michaelis, *Ber.* 1893, **26**, 2190) is a useful reagent for carbonyl compounds and particularly for sugars (Neuberg, *ibid.* 1899, **32**, 2395; *Z. physiol. Chem.* 1900, **29**, 256; microchemical use, Feigl, *Mikrochim. Acta*, 1937, **1**, 127; Wagenaar, *Pharm. Weekblad*, 1934, **71**, 229).

#### *p*-Nitrophenylhydrazine,



m.p. 157°. *p*-Nitraniline is diazotised, the diazonium salt reduced by alkali bisulphite and the resulting  $\alpha\beta$ -disulphonic acid hydrolysed by mineral acid (Bamberger and Kraus, *Ber.* 1896, **29**, 281; cf. G.P. 62004). The sparing solubility of *p*-nitrophenylhydrazones has been utilised in the estimation of aldehydes (Feinberg, *J. Amer. Chem. Soc.* 1927, **49**, 105), and of acetone in urine (Dehio, *Z. anal. Chem.* 1936, **104**, 417); for chemical use, see Feigl (*Mikrochim. Acta*, 1937, **1**, 127).

#### 2:4-Dinitrophenylhydrazine,



m.p. 198°, is best obtained by the interaction of 2:4-dinitro-chloro- or -bromo-benzene with hydrazine in alcoholic solution. It yields an orange pigment, m.p. 298°, on heating with acetacetanilide in alcohol (G.P. 269665) and is a valuable reagent for carbonyl groups (see HYDRAZONES) both for qualitative and quantitative purposes, e.g. for estimating furfural and camphor in galenical preparations (Hampshire and Page, *Quart. J. Pharm.* 1934, **7**, 558). Its use according to the original method of Brady (*J.C.S.* 1931, 756) sometimes gives rise to hydrazones of slightly varying melting-point, a phenomenon at one time ascribed to stereoisomerism but believed by Campbell (*Analyst* 1936, **61**, 391) to be due to aldol condensation products. This worker re-examined the melting

points of dinitrophenylhydrazones of approximately 100 aldehydes and ketones and recommends their preparation in isopropyl alcohol using hydrochloric acid.

**Methylphenylhydrazine**,  $\text{H}_2\text{N}\cdot\text{NMePh}$ , m.p. 131°/35 mm., is best prepared by reducing *N*-nitrosomethylaniline with zinc dust (Fischer, *Annalen*, 1886, **236**, 198) or electrolytically (Wells, Babcock and France, *J. Amer. Chem. Soc.* 1936, **58**, 2630). This base is useful for identifying sugars in particular, the hydrazones and osazones being crystallised from glycerol (Wagenaar, *Pharm. Weekblad*, 1934, **71**, 229). Methylphenylhydrazine heated with dihydroxy-naphthalenes, yields hydroxynaphthocarbazoles used as intermediates for azo colours (G.P. 548819).

**Diphenylhydrazine**,  $\text{H}_2\text{N}\cdot\text{NPh}_2$ , m.p. 44°, prepared by reducing *N*-nitrosodiphenylamine (Fischer, *Annalen*, 1878, **190**, 175; Stabel, *ibid.* 1890, **258**, 243), may be used to characterise simple aldehydes but is most valuable as a reagent for reducing sugars with which it gives beautifully crystalline hydrazones. Its use as an antioxidant in gasoline and in petroleum cracking distillates has been claimed (U.S.P. 1906044, 1793635).

#### Benzylphenylhydrazine,



b.p. 216–218°/38 mm., is prepared by the action of benzyl chloride on phenylhydrazine. When free from phenylhydrazine it reacts with sugars to give only hydrazones and not osazones.

**$\beta$ -Naphthylhydrazine**,  $\text{NH}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7(\beta)$ , m.p. 124–125°, is made by reducing  $\beta$ -naphthyl diazonium salts (Fischer, *Annalen*, 1886, **232**, 242) or by the action of hydrazine on  $\beta$ -naphthol in a sealed tube (Franzen, *Ber.* 1905, **38**, 266). This hydrazine forms highly crystalline, very sparingly soluble hydrazones, particularly with sugars, but it is remarkable that different products, probably stereoisomerides, are obtained when they are prepared in acetic acid or alcoholic solution (Hilger and Rothenfusser, *Ber.* 1902, **35**, 1841, 4444). Naphthocarbazoles may be obtained technically by heating naphthylhydrazine with hydroxynaphthalene carboxylic acids (U.S.P. 1948923).

A number of new chloro- and bromo-nitrophenylhydrazines and alkyl-aryl-hydrazines have been prepared by Maaskant (*Rec. trav. chim.* 1937, **56**, 211) by replacing halogen atoms in halogenonitrobenzenes by hydrazine, and representative hydrazones have also been described.

A. H. C.

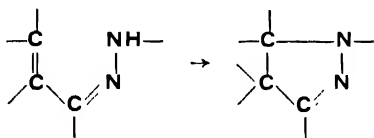
**HYDRAZOBENZENE**,  $\text{PhNH}\cdot\text{NHPh}$ , is prepared by reducing nitrobenzene in hot alcoholic solution with zinc dust or iron in presence of alcohol or solvent naphtha, and also by electrolysis. M.p. 126–127° (Darmstädter, G.P. 189312; *Chem. Zentr.* 1907, **II**, 2002; Ismailski and Kolpenski, *ibid.* 1933, **II**, 3049). Decomposes at the melting-point to give aniline and azobenzene. Hydrochloric acid converts it into benzidine.

**HYDRAZOIC ACID** (v. Vol. I, 580a).

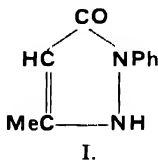
**HYDRAZONES.** Compounds obtained by eliminating water between carbonyl compounds and hydrazine or mono- or unsym.-disubstituted hydrazines :



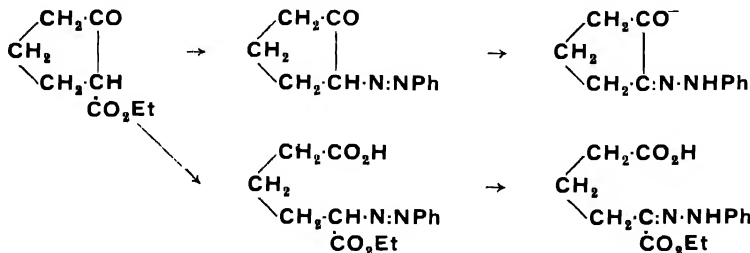
Simple mono-carbonyl compounds react with hydrazine itself under mild conditions to give monohydrazones, or azines,  $\text{R}'\text{RC}:\text{N}\cdot\text{N}\cdot\text{CRR}'$ , according to the proportion of base employed. On the other hand polycarbonyl compounds (e.g. benzil) usually afford polyhydrazones although 1:3- and 1:4-diketones react with hydrazine itself to give pyrazoles and pyrazines respectively and  $\beta$ -ketoesters react smoothly to give pyrazolones (cf. Fusco and Justoni, *Gazzetta*, 1937, **67**, 3), sometimes with intermediate formation of true hydrazones which can be isolated; dihydropyrazoles (pyrazolines) are often obtained from  $\alpha\beta$ -unsaturated carbonyl compounds in addition to unsaturated hydrazones (Raiford and Peterson, *J. Org. Chem.* 1937, **1**, 544) :



An important technical application of such reactions is the interaction of ethyl acetoacetate with phenylhydrazine when the first-formed phenylhydrazone loses a molecule of alcohol to give (I), the N-methyl derivative of which is the drug "antipyrine."

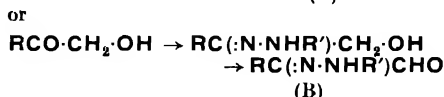
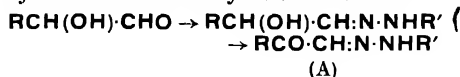


The substituted hydrazones of carbohydrates are readily oxidised by excess of the hydrazine, an adjacent  $-\text{CH}\cdot\text{OH}$  group being oxidised to



Among aromatic compounds the question of hydrazone or azo structure has given rise to discussion extending over many years. Zincke

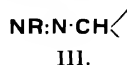
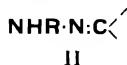
a  $-\text{CO}$  group which condenses with the hydrazine to form a dihydrazone or osazone :



Whilst the mono-hydrazones of sugars are appreciably soluble in water the osazones often crystallise well from water or very dilute acetic acid, and their characteristic crystalline forms serve as a ready means of identifying sugars microscopically (*v. infra*).

All of these compounds are normally obtained by interaction of the components in cold or warm alcoholic, aqueous or weakly acid solution.

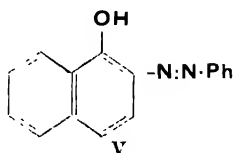
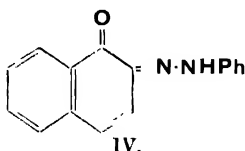
*Constitution.*—Whilst hydrazones derived from bases  $\text{NRR}'\cdot\text{NH}_2$  can only have the constitution  $\text{NRR}'\cdot\text{N}\cdot\text{CR}''\text{R}'''$ , a number of alternative structures have been proposed for the derivatives of primary hydrazines,  $\text{NHR}\cdot\text{NH}_2$ , e.g.



Although there is known to be a close connection between hydrazones (II) and azo-compounds (III) all normal hydrazones are believed to be of form (II). In other cases the problem is not easily decided. Thus many compounds which may be regarded as hydrazones are obtainable by the action of diazonium salts on phenols or compounds with reactive methylene groups. Hydrindene-1:3-dione gives a "hydrazone" which is hydrolysed to ninhydrin (1:2:3-triketohydrindene) and  $\beta$ -ketoesters exhibit similar reactions, usually with "acid" or "ketonic" hydrolysis (Japp and Klingemann, *Ber.* 1887, **20**, 2942, 3284, 3398; Annalen, 1888, **247**, 190). So ethyl cyclopentanone- and -hexanone-2-carboxylates yield with phenylhydrazine, dione monophenylhydrazones or phenylhydrazones of acyclic keto-acids according to the conditions (Linstead and Wang, *J.C.S.* 1937, 808; see also Dieckmann, *Annalen*, 1901, **317**, 27; Lyons, *J. Proc. Roy. Soc. New South Wales*, 1932, **66**, 516; Manske and Robinson, *J.C.S.* 1927, 240) :

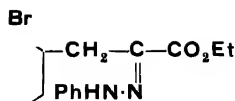
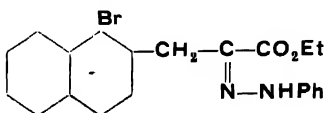
and Bindewald (*Ber.* 1884, **17**, 3026) studied the monophenylhydrazone of  $\alpha$ -naphthoquinone (IV) and observed that the same compound is ob-

tained from  $\alpha$ -naphthol and benzene diazonium chloride and might be thought therefore to possess structure (V):

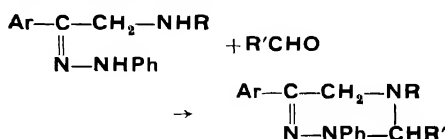


Many similar instances among *o*- and *p*-hydroxy-azo-compounds have since been noted. The evidence in favour of one or the other form in these instances is conflicting and ranges, for example, from the formation by *o*-hydroxyazo-compounds of chelate bodies in support of the azo structure to their unwillingness to form alkali metal salts as would be anticipated from a hydrazone structure. The chemical evidence has been summarised by Auwers (Annalen, 1931, 487, 79; 1933, 505, 283), who concludes on this basis that the *p*-compounds are azo bodies whilst their *o*-isomers behave as *o*-quinonoid derivatives. Kuhn (Naturwiss. 1932, 20, 622) had suggested a betaine structure, but his later spectroscopic evidence (Kuhn and Bär, Annalen, 1935, 516, 143) indicates that the two forms are in equilibrium in solution, one or other form predominating according to the solvent; this interpretation, however, is not wholly accepted by Burawoy (*ibid.* 1936, 521, 298; J.C.S. 1936, 36). (For a review of the spectrochemistry of hydrazones, see Ramart-Lucas, Bull. Soc. chim. 1936, [v], 3, 723).

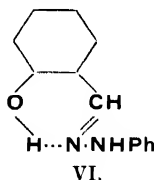
Hydrazones of the form  $CRR':N:NR''R'''$ , where  $R, R'$  are different, are theoretically capable of existing in two stereochemical modifications according to the direction of the  $N:N$  linkage with respect to the double bond and a large number of isomers of this type are known (see Meisenheimer and Thielacher in Freudenberg's "Stereochemie," 1933, p. 1095); quite stable isomers of certain di- and tri-nitrophenylhydrazones (e.g. of furfural) have been prepared (Bredereck and Fritzsche, Ber. 1937, 70 [B], 802) and Sempronj (Gazzetta, 1938, 68, 263) starting with 1:2-bromonaphthylmethyl bromide prepared ethyl  $\alpha$ -acetyl- $\beta$ -(1-bromo-2-naphthyl) propionate, which on hydrolysis and treatment with benzene diazonium chloride gave two isomers of 1-bromo-2-naphthyl-pyruvic acid phenylhydrazone which must be regarded as stereoisomers as each gives rise to the same indole by the Fischer reaction:



In these instances the configuration is rarely established with certainty as no general reaction is known to afford any distinction such as does the Beckmann rearrangement in the case of stereoisomeric oximes; isomeric phenylacetylene hydrazones have been distinguished by the ability of one isomer to form cyclic condensation products with aldehydes



(Busch, Friedenberger and Tischbein, Ber. 1924, 57 [B], 1785) and similar arguments have been advanced with reference to stannic chloride addition compounds of benzilosazones (Hieber and Sonneckalb, Annalen, 1927, 456, 86). The fact that no absorption in the infra-red spectra of *o*-hydroxyarylhydrazones can be traced to hydroxyl groups has suggested that chelation normally exists. This can be so only, for example, in salicylaldehyde phenylhydrazone (VI), when the configuration of the aryl and  $-\text{NHPh}$  groups about the  $\text{C}=\text{N}$  linkage is *trans*,



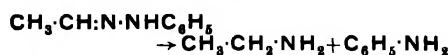
and indeed if experience of azo compounds is a guide then this is the normal or more stable configuration of all hydrazones.

**Properties.**—Hydrazones are usually well crystallised compounds, particularly when derived from arylhydrazines. On warming with mineral acid they are relatively smoothly hydrolysed to the parent carbonyl compounds, but regeneration is more conveniently effected by "double decomposition" using pyruvic acid:



(Fischer and Ach, *ibid.* 1889, 253, 57). Difficulties in regeneration, particularly of ketones, have been recently overcome by the use of tertiary ammonium acethydrazides, Girard's Reagents (*q.v.*).

Mild catalytic reduction of phenylhydrazones by hydrogen in presence of palladium affords substituted hydrazines whilst more drastic reduction results in rupture of the  $\text{N:N}$  bond with formation of a mixture of amines:



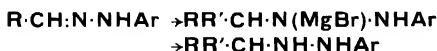
Oxidation of hydrazones with iodine, amyl nitrite or mercuric oxide (Von Pechmann, Ber. 1893, **26**, 1045) yields tetrazanes (hydrotetrazanes). In some instances (Curtius, J. pr. Chem. 1891, [ii], **44**, 182, 200, 535), however, the products do not contain 4 atoms of nitrogen but are true diazo-compounds (Forster and Zimmerli, J.C.S. 1910, **97**, 2156; Staudinger and Kupfer, Ber. 1911, **44**, 2197), this providing a convenient method for their preparation. Thus benzo-phenonehydrazone and mercuric oxide yield diphenyldiazomethane,  $(C_6H_5)_2CN_2$  (Staudinger, Anthes and Pfenniger, *ibid.* 1916, **49**, 1932).

Many hydrazones lose ammonia when treated with zinc chloride or often with hot dilute mineral acid to yield indoles (*q.v.*), although normal regeneration takes place in some instances and cold strong hydrochloric acid will normally hydrolyse osazones to the diketones.

The imino hydrogen atom of phenylhydrazones reacts with maleic anhydride with the formation of substituted maleiamido-acids; in isolated instances these might be of value as a further means of characterising the hydrazones (Parola, Gazzetta, 1935, **65**, 624).

Hydrazones may be oxidised by selenious acid into diazonium salts which may be detected in amounts as little as 0.04  $\mu$ g. by conversion into azo-colours, the reaction therefore affords a sensitive test for hydrazones (Feigl, Mikrochim. Acta, 1937, **1**, 127).

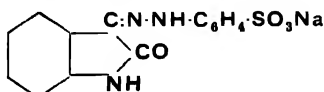
Arylhydrazones of aliphatic aldehydes react with Grignard reagents; the addition compounds may be decomposed to give hydrazines and so provide a useful source of substituted bases (Grammaticakis, Compt. rend. 1937, **204**, 1262):



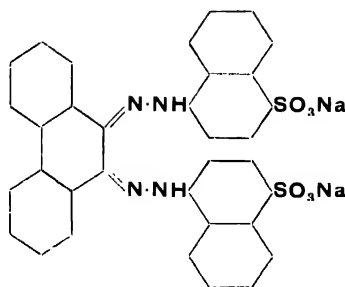
This last reaction is similar to the direct addition of HCN to hydrazones to form nitriles (*cf.* Miller and Plöchl, Ber. 1892, **25**, 2023).



*Application.*—Hydrazones have not found direct extensive industrial application, although the use, for example, of sulphonated arylhydrazones as a source of sulphonated indoles is the subject of patent claims (B.P. 340619). The derived pyrazolones are represented by some drugs ("antipyrene") and by an important group of dyestuffs in which tartrazine (*v. p.* 301a) may be regarded as a hydrazone (*v. HYDRAZINES*, this Vol., p. 298c). Isatin Yellow (VII), obtained by the action of phenylhydrazine-*p*-sulphonic acid on isatin (G.P. 40476), and Phenanthrene Red (VIII) from phenanthraquinone and 1-naphthylhydrazine-4-sulphonic acid (G.P. 40745) are probably true hydrazones.

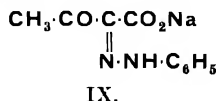


VII.



VIII.

The  $\text{>C} \text{--} \text{N}$  linking in the hydrazones gives rise to considerable absorption of light of  $\lambda$  3,500–3,700Å. and it has been proposed to utilise this property in more highly substituted hydrazones such as (IX) in the construction of ultra-violet light filters (U.S.P. 2129132).



In the laboratory hydrazones, usually aryl compounds, provide a ready means of characterising and, in some cases, of estimating carbonyl compounds. Phenylhydrazones are commonly employed, but *p*-nitro- and *p*-bromo-phenylhydrazones,  $\beta$ -naphthyl-, methyl-phenyl-, and asym. diphenylhydrazones are also used. The 2:4-dinitrophenylhydrazones crystallise well and are valuable (Brady *et al.*, Analyst, 1926, **51**, 77; J.C.S. 1929, 478; 1931, 756; Allen, J. Amer. Chem. Soc. 1930, **52**, 2955); owing to the ease with which they are obtained in alcoholic sulphuric acid or hydrochloric acid solution and their relative insolubility, they can, in some instances, be isolated quantitatively (Iddles and Jackson, Ind. Eng. Chem. [Anal.], 1934, **6**, 454). Instances have been recorded, *e.g.* the complex ketones tetracyclone, accecyclone, etc., where the commoner hydrazones are unobtainable but where 2:4-dinitrophenylhydrazones have formed normally (Josten, Ber. 1938, **71** [B], 2230). Nitroguanylhydrazones (Smith and Shoub, J. Amer. Chem. Soc. 1937, **59**, 2077) and *m*-tolyl- (Sah and Tseu, Sci. Rep. Nat. Tsing Hua Univ. 1936, **3**, 403) have also been recommended for this purpose.

Some sugars can be identified by examining under the microscope the crystalline form of their osazones (*v. supra*) with phenyl-, tolyl- and other hydrazines (*see* Sah and Tseu, *ibid.* 409; Fischer and Paulus, Arch. Pharm. 1935, **273**, 83).

A. H. C.

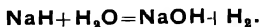
**HYDRAZOTOLUENES**, prepared by suitable reduction of the corresponding nitrotoluene. *oo'*-Hydrazotoluene, m.p. 156° (Rassow and Becker, J. pr. Chem. 1911, [ii], **84**, 335; G.P. 297019; U.S.P. 1225052). *mm'*-Hydrazotoluene is a yellow oil. *pp'*-Hydrazotoluene, m.p. 134° (Rassow and Rülke, J. pr. Chem. 1902, [ii], **65**, 120, 108).

**HYDRIDES.** The hydrides, which include a number of the commonest inorganic compounds as well as some of those most difficult to prepare, may be classified as follows:—

- (a) Volatile hydrides.
- (b) Salt-like hydrides.
- (c) Solid hydrides of ill-defined composition, which are probably interstitial compounds (*v. infra*).
- (d) Certain other hydrides which cannot readily be included in classes (a)–(c).

(a) **Volatile Hydrides.**—The most versatile hydride-forming element is carbon; organic chemistry may be regarded as the chemistry of carbon hydrides and their derivatives, which are, in general, to be assigned to the class of volatile hydrides. Other elements giving hydrides of this type are as follows: boron (Vol. II, 40*d*); silicon; germanium (Vol. V, 521*d*); tin (Paneth *et al.*, Ber. 1919, 52 [B], 2020); lead (*idem*, *ibid.* 1920, 53 [B], 1693); nitrogen (*v.* AMMONIA, HYDRAZINE, AZOIMIDE); phosphorus; arsenic (Vol. I, 472*d*); antimony; bismuth (Vol. I, 699*b*); oxygen (*v.* HYDROGEN PEROXIDE); sulphur, selenium, tellurium, polonium; fluorine (Vol. V, 278*d*); chlorine (Vol. III, 69*a*), bromine (Vol. II, 117*a*), and iodine. It will be noted that formation of volatile hydrides is generally characteristic of non-metals, although a few metallic elements also give hydrides of this type. The linkings in volatile hydrides are usually covalent (*v.* COORDINATION COMPOUNDS).

(b) **Salt-like Hydrides.**—The known salt-like hydrides (*viz.* LiH, NaH, KH, RbH, CsH (Vol. II, 196*c*), CaH<sub>2</sub> (Vol. II, 205*d*), SrH<sub>2</sub> and BaH<sub>2</sub>) are white crystalline solids, generally prepared by heating the metal in hydrogen; for the preparation and properties of barium hydride, *see* Guntz, *Compt. rend.* 1901, 132, 963; Dafert and Miklausz, *Monatsh.* 1913, 34, 1685. These hydrides are probably similar in constitution to salts of the metals, since (i) the alkali-metal hydrides have crystal lattices similar to that of sodium chloride; (ii) on electrolysis of the fused hydrides the metal is liberated at the cathode and hydrogen at the anode (Kasarnowsky, *Z. anorg. Chem.* 1928, 170, 311; Peters, *ibid.* 1923, 131, 140); (iii) the hydrides are exothermic and denser (*cf.* class (c)) than the parent metals (Sieverts and Gotta, *ibid.* 1928, 172, 1; Hagen and Sieverts, 1930, 185, 239, 254; Proskurnin and Kasarnowsky, *ibid.* 1928, 170, 301). The salt-like hydrides react readily with water, affording hydrogen and the metallic hydroxide, *e.g.*



(c) **Interstitial Hydrides.**—Certain metals absorb relatively large quantities of hydrogen when heated in the gas and give ill-defined solid “hydrides,” the exact composition of which varies with the conditions of preparation. Typical products of this type may be represented by the following non-stoichiometric formulae, which merely serve to show the ratio between the numbers of metal and hydrogen atoms in the crystal lattices of the solid

hydrides: LaH<sub>2.70</sub>, CeH<sub>2.60</sub> (given in Vol. II, 508*c*, as “CeH<sub>2</sub> (?)”), PrH<sub>2.55</sub>, ZrH<sub>1.92</sub>, TiH<sub>1.73</sub>, ThH<sub>2.07</sub>, VH<sub>0.58</sub>, TaH<sub>0.76</sub> and PdH<sub>0.6</sub> (Hagen and Sieverts, *ibid.* 1928, 185, 225; Sieverts and Gotta, *ibid.* 1928, 172, 1; 1930, 187, 155; 1931, 199, 384; *Z. Elektrochem.* 1928, 32, 105; Sieverts and Roell, *Z. anorg. Chem.* 1926, 153, 289; Huber, Kirschfeld and Sieverts, Ber. 1926, 59 [B], 2801). As in the case of the salt-like hydrides, heat is evolved when these substances are formed from their elements; the interstitial hydrides, however, are less dense than the parent elements (Sieverts and Gotta, *l.c.*). This fact supports the view that the hydrogen atoms are accommodated in the interstices of the metal lattice, which is expanded by the insertion of these atoms. The interstitial hydrides are powerful reducing agents, probably because the loosely-held hydrogen which they contain is in the atomic condition.

The amount of hydrogen adsorbed by metals such as iron, cobalt, nickel and platinum is insufficient to indicate formation of interstitial hydrides comparable with those cited above, but the mechanism of the adsorption process is probably similar to that of the formation of these hydrides (*cf.* HYDROGEN—Adsorption).

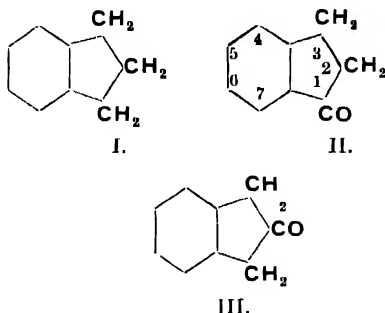
(d) **Other Hydrides not Classified Above.**—A copper hydride containing rather less hydrogen than is indicated by the formula CuH is precipitated on addition of sodium hypophosphite solution to a solution of cupric sulphate at 65°. Copper hydride is a brown explosive powder when freshly prepared, but it becomes black and more stable on keeping (Neunhoeffer and Nerdel, *J. pr. Chem.* 1935–36, [u], 144, 63). It is an endothermic compound, the heat of formation being –5.12 kg.-cal. (Sieverts and Gotta, *Annalen*, 1927, 453, 289). Solid hydrides of nickel, cobalt, iron and chromium, NiH<sub>2</sub>, CoH<sub>2</sub>, FeH<sub>2</sub> and CrH<sub>3</sub>, are precipitated on passing hydrogen through an ethereal solution of phenyl magnesium bromide containing the appropriate anhydrous metal chloride in solution or suspension; another iron hydride prepared by a similar method, FeH<sub>6</sub>, is described as a heavy oil (Weichselder and Thiede, *ibid.* 1926, 447, 64). There is evidence for the existence of a tungsten compound of a similar type (*idem*, *ibid.*).

Further details relating to hydrides will be found in articles dealing with the individual elements. For a general review, *see* Emeléus and Anderson, “Modern Aspects of Inorganic Chemistry,” London, 1938.

**HYDRINDONE, Indanones.** From the structure of hydrindene (I) it is evident that it is the parent substance of two cyclic mono-ketones, two di-ketones and one tri-ketone.

*a-Hydrindone* (Indan-1-one) (II) has been prepared from  $\beta$ -phenylpropionyl chloride (25 g.) in light petroleum (40 g.) by the action of aluminium chloride (25 g.) with gentle warming for  $\frac{1}{2}$  hour (Kipping, *J.C.S.* 1894, 65, 485). Wedekind effected the condensation with ferric chloride in carbon disulphide solution (*Annalen*, 1902, 323, 255). Other modifications of the preparation from  $\beta$ -phenylpropionyl chloride have been devised (Thiele and Wanscheidt, *ibid.* 1910,

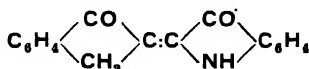
376, 271; Haller and Bauer, *Compt. rend.* 1910, 150, 1475; Ingold and Thorpe, *J.C.S.* 1919, 115, 149. It is also formed by dropping acrylyl chloride (20 g.) dissolved in benzene (34 g.) into a mixture of aluminium chloride (20 g.) and carbon disulphide (60 g.) (Moureau, *Bull. Soc. chim.* 1893, [iii], 9, 570; *Ann. Chim.* 1894, [vii], 2, 199; Kohler, *Amer. Chem. J.* 1909, 42, 375). R. A. Pacaud and C. F. H. Allen ("Organic Syntheses," 1938, 18, 47) add hydrogen chloride to freshly distilled indene, the resulting  $\alpha$ -chloroindene is then oxidised by chromic anhydride dissolved in diluted acetic acid (1:1) at 35–40°. After dilution and neutralisation with sodium carbonate, the hydrindone is recovered by steam distillation.



$\alpha$ -Hydrindone is colourless and crystalline, m.p. 39–42° (different observers), b.p. 243–245° (Gabriel and Hausmann, *Ber.* 1889, 22, 2018),  $d$  about 1.1, magnetic rotation (Perkin, *J.C.S.* 1894, 65, 489; 1896, 69, 1243).

On halogenation, the hydrogen atoms in position 2 are first replaced, then those in position 3. The oxime has m.p. 144°; azine, m.p. 164–165°; semicarbazone, m.p. 239° (or 233°); and *p*-nitrophenylhydrazones, m.p. 234–235°. The keto-group is also capable of reacting with active methylene groups, thus Thorpe and Ingold obtained ethyl indenyl-3-cyanoacetate by condensation with ethyl cyanoacetate in presence of secondary bases (*J.C.S.* 1919, 115, 150).

The carbonyl group activates the methylene group in position 2 so that 2 mol. of  $\alpha$ -hydrindone condense to give anhydro-bis- $\alpha$ -hydrindone (Kipping, *l.c.*, p. 495); whilst both methylene groups react with *p*-nitrosodimethylaniline (Ruhemann, *J.C.S.* 1910, 97, 1445). With isatin chloride, 2:2'-indoxylindan-1-one,



is formed (Felix and Friedlaender, *Monatsh.* 1910, 31, 60; Kalle and Co., G.P. 227862).

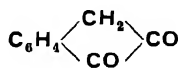
$\beta$ -Hydrindone (Indan-2-one) (III) has been obtained by distillation of calcium *o*-phenylene-diacetate (Schad, *Ber.* 1893, 26, 222; Benedikt, *Annalen*, 1893, 275, 353), by heating hydrindene glycol with dilute sulphuric acid (Heuser and Schieffer, *Ber.* 1899, 32, 30) and from 2-nitroindene which is reduced to  $\beta$ -hydrindone oxime

(zinc dust and acetic acid) and then hydrolysed by dilute sulphuric acid (Wallach and Beschke, *Annalen*, 1904, 336, 3). Moore and Thorpe obtained the compound by the action of sulphuric acid on 2-aminoundene-3-carboxylic acid which reacts as 2-imino-hydrindene-3-carboxylic acid (*J.C.S.* 1908, 93, 186; see also *Proc. C. S.*, 1911, 27, 108).

M.p. 58° or 60°; b.p. 220–225°. Oxime, m.p. 155°; semicarbazone, m.p. 218° (decomp.).

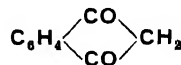
1:1:3:3-Tetrachloro- $\beta$ -hydrindone results from the action of bleaching powder on 1:1:4:4-tetrachloro-2:2-diketotetrahydronaphthalene (Zincke and Fries, *Annalen*, 1904, 334, 256).

$\alpha\beta$ -Diketohydrindene (Indan-1:2-dione),



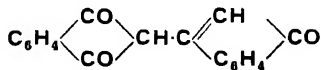
results when isonitroso- $\alpha$ -hydrindone is hydrolysed by hydrochloric acid in presence of formaldehyde (Perkin, Roberts and Robinson, *J.C.S.* 1912, 101, 232; see earlier papers, Kipping, *ibid.* 1894, 65, 492; Gabriel and Stelzner, *Ber.* 1890, 29, 2604. Cf. also Steinkopf and Besaritsch, *ibid.* 1914, 47, 2931).

$\alpha\gamma$ -Diketohydrindene (Indan-1:3-dione),

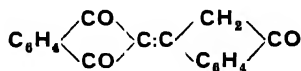


Acetic and phthalic esters are condensed by sodium ethoxide, the resulting diketohydrindene carboxylic ester hydrolysed and carbon dioxide eliminated from the resulting acid. M.p. 129–131° (Gabriel and Neumann, *ibid.* 1893, 26, 954; G. Ponzio and A. Pichetto, *Gazzetta*, 1923, 53, 20; W. O. Teeters and R. L. Shriner, *J. Amer. Chem. Soc.* 1933, 55, 3026).

The methylene group is very reactive and anhydrodiketohydrindone is produced by elimination of water between 2 mol. (Wislicenus and Kötze, *Annalen*, 1889, 252, 76). According to Hantzsch (*ibid.* 1912, 392, 322), anhydrodiketohydrindone is



and not



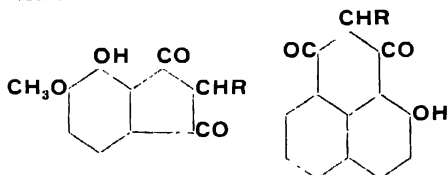
Cf. also Fischer and Wanag (*ibid.* 1931, 489, 97).

The reactivity of the methylene group is also exhibited in the reaction with phenyldiazonium salts which give triketohydrindene  $\beta$ -phenylhydrazones.  $\alpha\gamma$ -Diketohydrindene also condenses with isatin chloride to give 2:2'-indoxylindan-1:3-dione, a compound of indigoid type (Felix and Friedländer, *Monatsh.* 1910, 31, 55).

Derivatives of indan-1:3-dione have been prepared by Black, Shaw and T. K. Walker (*J.C.S.* 1931, 272), and Walker, Suthers, Roe and Shaw (*ibid.*, p. 514). Malonyl chloride and several alkyl substituted malonyl chlorides,  $\text{R} \cdot \text{CH}(\text{COCl})_2$  ( $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, n\text{-C}_5\text{H}_{11}$ ,

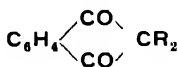


$n\text{-C}_6\text{H}_{13}$ ,  $n\text{-C}_7\text{H}_{15}$ ,  $iso\text{-C}_7\text{H}_{15}$ ,  $iso\text{-C}_8\text{H}_9$ ,  $iso\text{-C}_8\text{H}_{11}$ ) and  $(\text{C}_6\text{H}_5)_2\text{C}(\text{COCl})_2$  have been condensed with resorcinol dimethyl ether and with  $\beta$ -naphthyl methyl ether by aluminium chloride in nitrobenzene solution. Demethylation occurs in the *ortho*-position to carbonyl and the resulting compounds have the following structures:



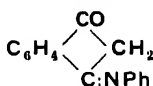
The numerous derivatives prepared in this way have been studied with respect to their antiseptic powers, which are selective.

Numerous compounds of the type

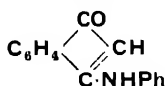


have been synthesised by Freund and Fleischer (Annalen, 1913, **399**, 182; 1913, **402**, 51; 1915, **409**, 268; 1917, **414**, 1), Das and Ghosh (J. Amer. Chem. Soc. 1919, **41**, 1221), Fleischer (Annalen, 1921, **422**, 231, 265, 272, 317).

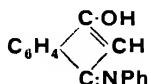
Such disubstituted diketohydrindenes must necessarily possess a diketonic structure, but *enol* tautomerism is possible in the case of the parent substance and certain derivatives. Thus the *anil* (m.p.  $208^\circ$ ) is probably



in the free state, whilst the salts with acids and bases are probably derived from the forms

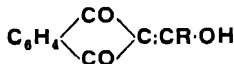


and



respectively

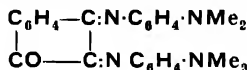
The enolisation of 2-monoacylindan-1:3-diones may give compounds of the type



(Scheiber and Hopfer, Ber. 1920, **53** [B], 697).

*Triketohydrindene*, Indanetrione,  $\text{C}_9\text{H}_6\text{O}_3$ . *Hydrate*,  $\text{C}_9\text{H}_6\text{O}_4$ . When diphtalylethane is oxidised with hydrogen peroxide, diphtalylethylene ("indenigo") is obtained as the chief product of the reaction (v. Kaufmann, *ibid.* 1897, **30**, 387). A small amount of a by-product was isolated, which was supposed to be triketohydrindene but the amount was insufficient for analysis.

Ruhemann subsequently isolated the triketone as its colourless hydrate and examined its reactions (J.C.S. 1910, **97**, 1438, 1446, 2025). For the preparation, use is made of the fact that both the methylene groups of  $\alpha$ -hydrindone react with *p*-nitrosodimethylaniline. Solutions of 6 g. of the former and 24 g. of the latter, each in 50 c.c. alcohol, are mixed, cooled with ice and a small quantity of alcoholic potash added. After a day, the black solid is collected and crystallised from a large quantity of methylated spirit. The product forms green prisms (solution, bluish-black), m.p.  $174^\circ$ , it is the hydrate of 2:3-bis (*p*-dimethylaminoanilo)- $\alpha$ -hydrindone:

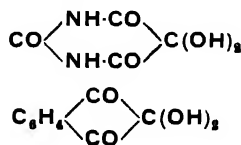


By gently warming with dilute sulphuric acid, triketohydrindene hydrate is liberated (*ibid.*). On crystallisation from hot water, colourless prisms are obtained which turn red at  $125^\circ$ , froth at  $139^\circ$  and decompose at  $239\text{--}240^\circ$ . Ruhemann also prepared the hydrate from 1:3-diketohydrindene and from  $\beta$ -hydrindone using nitrosodimethylaniline and hydrolysing the resulting anils (J.C.S. 1911, **99**, 796; cf. Pfeiffer and Hesse, J. pr. Chem. 1941 [ii], **158**, 315). It is also obtained in 31–35% yield from 1:3-diketohydrindene and  $\text{SeO}_2$  in aqueous dioxan (W. O. Teeters and R. L. Shriner, J. Amer. Chem. Soc. 1933, **55**, 3026).

For the absorption spectrum, see Purvis, J.C.S. 1911, **99**, 1953. The alkaline solution is yellow at first, becoming colourless, at which stage it contains *o*-hydroxymandelic acid. The aqueous solution reduces Fehling's and ammoniacal silver solutions but is itself reduced to 2-hydroxy-1:3-diketohydrindene by sodium amalgam. The substance is markedly poisonous.

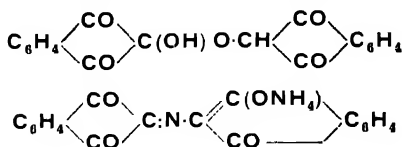
Under the name of *ninhydrin*, triketohydrindene hydrate has found application as a reagent. It had been observed that the compound gave a deep blue coloration with amino-acids by means of which mere traces of the hydrolytic products of proteins could be recognised (Ruhemann, J.C.S. 1910, **97**, 2025; 1911, **99**, 793, 1486). The presence of free amino- and carboxyl-groups was necessary for a positive result.

Comparison of the formulæ of alloxan and ninhydrin:



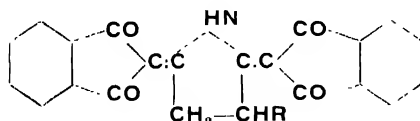
suggests that as alloxan reacts with amino-acids to give an aldehyde and murexide (Strecker; Annalen, 1862, **123**, 363), so the triketohydrindene may act as an oxidising agent on amino-acids giving an aldehyde, carbon dioxide and ammonia, the last of these compounds then reacting with the "hydrindantin" formed by the reduction of the ninhydrin with formation of an ammonium salt of diketohydrindylidenediketohydrindamine. Hydrindantin was obtained by the reduction of ninhydrin with hydrogen

sulphide and gave the expected reactions; its formula and that suggested for the product from ninhydrin and ammonia are as follows:



It was found that not only the  $\alpha$ -amino-acids but also acids with an amino-group in  $\beta$ -,  $\gamma$ -,  $\delta$ -, or  $\epsilon$ -positions respond to the test. Ruhemann states that both amino- and carboxyl-groups must be intact so that the reaction is not given by phenylglycine or hippuric acid or by the esters of the amino-acids. Ruhemann found that the test was so delicate that when hydrindantin is boiled with alcohol, it gradually dissolves to yield a dark reddish-violet solution. This was attributed to ammonia present in the air of the laboratory, and precautions should therefore be taken (H. Gardner, *Lancet*, 1930, ii, 525).

Condensation of ninhydrin with proline can be effected in aqueous solution at  $p_{\text{H}}$  7. The products from proline and hydroxyproline have been assigned the constitutions ( $\text{R}=\text{H}$  or  $\text{OH}$ ) (W. Grassmann and K. von Arnim, *Annalen*, 1934, 509, 288).



(Numerous references to the use of ninhydrin as a reagent will be found in the biochemical literature.)

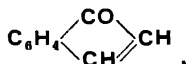
#### Oximes of triketohydrindene:

2-Monoxime, m.p. 200–201° (decomp.). Obtained from 1:3-diketohydrindone and nitrous acid (W. O. Teeters and R. L. Shriner, *J. Amer. Chem. Soc.* 1933, 55, 3026).

1:3-Dioxime, m.p. 233° (decomp.). By adding amyl nitrite (10 g.) and  $\text{HCl}$  (1 c.c. 30%) to 2-hydrindone (4.5 g.) in alcohol (15 c.c.) (F. Heusler and H. Schieffer, *Ber.* 1900, 33, 32).

1:2-Dioxime, m.p. 168° (decomp.). From 2-oximino-1:3-diketohydrindone, hydroxylamine hydrochloride and sodium acetate in alcohol at 60–70°. ( $\text{C}_6\text{H}_5\text{O}_3\text{N}_2$ )<sub>2</sub>Ni and other derivatives have been prepared (G. Ponzio and A. Pichetto, *Gazzetta*, 1923, 53, 1, 20).

#### Indenone,

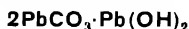


Some halogen substituted derivatives have been made (Zincke, *Ber.* 1887, 20, 1269; Schlossberg, *ibid.* 1900, 33, 2426).

J. T. H.

**HYDROCERUSSITE.** Until recently this mineral was known only from two localities in Scotland and Sweden as very thin, scaly crusts with pearly lustre on oxidized lead ores. The

Scotch mineral had from its appearance been named "plumbonacrite." Analyses of the very small amount of material had given different results, and the formula



was based on analyses of the artificially prepared crystalline material (L. Bourgeois, 1888). Later it was recognised on specimens from the ancient lead mines in the Mendip Hills in Somersetshire, the best material having been preserved in the mineral collection of John Woodward, which was bequeathed to the University of Cambridge in 1728. In the Mendip lead ores the mineral usually occurs as an intermediate stage in the alteration of mendipite ( $2\text{PbO} \cdot \text{PbCl}_2$ ) to cerussite ( $\text{PbCO}_3$ ). Crystals are rhombohedral with a tabular or lenticular (flat rhombohedral) habit, and are characterised by a perfect basal cleavage on which the lustre is markedly pearly. On a cross fracture the mineral closely resembles cerussite in appearance, for which it has no doubt often been mistaken. Cleavage flakes are optically uniaxial and negative; sp.gr. 6-80, hardness 3½. Analyses of the Mendip mineral show the presence of a small amount (0.3%) of chlorine, suggesting the presence of a compound  $2\text{PbCO}_3 \cdot \text{PbCl}_2$  in isomorphous mixture with  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . Hydrocerussite as minute scaly crystals has also been detected in Roman lead slags from Laurion in Greece and from the Mendip Hills (L. J. Spencer, *Min. Mag.* 1923, 20, 80).

Hydrocerussite is identical in composition with the white lead (Latin, cerussa) of commerce, and the purer flake-white no doubt owes its scaly form to the lamellar habit and the perfect basal cleavage of the crystalline material.

L. J. S.

**HYDROCHLORIC ACID** (v. Vol. III, 69).

**HYDROCINCHONICINE** (v. Vol. III, 163c).

**HYDROCINCHONIDINE** (v. Vol. III, 162a).

**HYDROCINCHONINE** (v. Vol. III, 162d).

**HYDROCINCHONINONE** (v. Vol. III, 163d).

**HYDROCINCHOTOXINE** (v. Vol. III, 163c).

**HYDROCUPREICINE** (v. Vol. III, 168a).

**HYDROCUPREIDINE** (v. Vol. III, 165c).

**HYDROCUPREINE** (v. Vol. III, 167c).

**HYDROCUPREINOTOXINE** (v. Vol. III, 168a).

**HYDROCYANIC ACID** (v. Vol. III, 492c).

**HYDROFLUORIC ACID.** Use of in etching glass (v. Vol. V, 281c).

**HYDROFLUOSILICIC ACID** (v. Vol. V, 282b).

#### HYDROGEN.

**History.**—The existence of a gas, which has since been shown to be predominantly hydrogen, was recognised in very early times. Its inflammability was noted by Van Helmont and by Turquet de Mayerne in the seventeenth century. It hence became known as "inflammable air" and was somewhat naturally confused with other inflammable gases such as

hydrocarbons, carbon monoxide and hydrogen sulphide.

Cavendish (Phil. Trans. 1766, **56**, 141) showed that in the reaction between dilute sulphuric or hydrochloric acids and iron, zinc or tin the same gas was liberated. He confirmed its combustibility, and measured its specific gravity and the amount of gas evolved relative to the amount of metal used. During most of the eighteenth century, however, the ideas on the nature of hydrogen were confused by the phlogiston theory.

**Occurrence.**—In the free state hydrogen occurs widely but in small quantities. To a very slight extent it occurs free in the atmosphere (Gautier, Ann. Chim. Phys. 1901, [vii], **22**, 5; Liveing and Dewar, *ibid.* p. 482; Rayleigh, Phil. Mag. 1902, [vi], **3**, 410; Leduc, Compt. rend. 1902, **135**, 860, 1332). According to Claude (*ibid.* 1909, **148**, 1454) there is less than 1 part of hydrogen in 1 million parts of air. It occurs in the upper atmosphere but is virtually absent from certain layers (Kaplan, Nature, 1935, **136**, 549; Pederson, Kgl. Danske Vidensk. Selsk. Math.-fys. Medd. 1927, **8**, No. 4; Amer. Chem. Abstr. 1928, **22**, 2873). It occurs in fumaroles in Tuscany and other places. The gases issuing from the salt beds of Stassfurt (Reichardt, Arch. Pharm. 1860, **103**, 347; Precht, Ber. 1880, **13**, 2326) and at Wdliczka (Rose, Pogg. Ann. 1839, **48**, 353) contain hydrogen, and it also occurs in the gases given off by the oil-wells of Pennsylvania, West Virginia, Ohio and Indiana (Engler, Ber. 1888, **21**, 1816; U.S.A. Geol. Sur. 1909, **2**, 297). Hydrogen has been found occluded in certain meteorites (Graham, Proc. Roy. Soc. 1867, **15**, 502; Mallet, *ibid.* 1872, **20**, 365), and in a large number of minerals (Ramsay and Travers, Proc. Roy. Soc. 1897, **60**, 442; Tilden, *ibid.* 1897, **60**, 453), and in clays. It occurs in the gaseous mixtures evolved from certain volcanos (Bunsen, Ann. Chim. Phys. 1853, [iii], **38**, 259; Deville, Compt. rend. 1862, **55**, 75).

Spectroscopic observations have shown that hydrogen completely surrounds the sun, forming an envelope which has received the name of the chromosphere. Hydrogen also occurs in certain stars and nebulae.

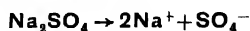
In a combined form hydrogen has even a wider distribution on the earth's surface than in the free state, and occurs much more abundantly. In the region comprising the earth's crust, the ocean and the atmosphere, hydrogen is the ninth most plentiful element from the point of view of weight (0.95%) and the second most plentiful element from the point of view of the number of atoms (16.3%) (Clarke, "The Data of Geochemistry," Washington, 1916, p. 34). The forms in which combined hydrogen occurs are well known: water and hydrates, acids, alkalis, hydrides, hydrocarbons and virtually all organic compounds.

#### FORMATION.

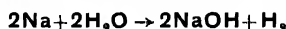
(1) **Electrolysis.**—If a dilute solution of an acid is electrolysed between electrodes which are unattacked by hydrogen, there is an evolution of hydrogen at the cathode as a primary decomposition product. Under comparable con-

ditions the electrolysis of a salt or alkaline solution yields hydrogen at the cathode as a secondary decomposition product. Thus with  $\text{Na}_2\text{SO}_4$ :

Primary decomposition,



Secondary decomposition at cathode, "



In dilute solutions of acids and of alkalis the final products are in both cases  $\text{H}_2$  and  $\text{O}_2$ , and the process is referred to as the electrolysis of water, since the acid or alkali decomposed by electrolysis is reformed by secondary decomposition and only the elements of water are removed from the reaction medium. The energy required for evolution of equivalent amounts of  $\text{H}_2$  and  $\text{O}_2$  (apart from over-voltage and the resistance of the solution) is thus independent of the electrolyte. The total energy required with smooth platinum electrodes was determined by Le Blanc (Z. physikal. Chem. 1891, **8**, 299; 1893, **12**, 333) as about 1.7 volts for *N*-solutions, which is thus the minimum voltage required for the electrolysis of water. Ideally 1 g.-equivalent of hydrogen (for that matter of any element) is liberated by 96,500 coulombs of electricity. In practice the amounts of hydrogen and oxygen evolved are not exactly equivalent to each other or to the amount of current. This is due to the different solubility of  $\text{H}_2$  and  $\text{O}_2$  in water, to recombination of  $\text{H}_2$  and  $\text{O}_2$  in solution, and (if a sulphuric acid solution is used) to the formation of persulphuric acid and to other minor causes.

Hydrogen is also evolved in the electrolysis of certain solutions where oxygen is not given off at the anode, e.g. in the electrolysis of acids such as  $\text{HCl}$  whose anion does not undergo secondary decomposition. Here the products are  $\text{H}_2$  and  $\text{Cl}_2$  and the decomposition voltage is about 1.31 volts for a *N*-solution.

In the electrolysis of solutions of certain salts of strong acids and strong bases, e.g.  $\text{Na}_2\text{SO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ , the final decomposition products are again hydrogen and oxygen. The secondary decomposition, however, results not in the re-formation of the neutral salt but of acid ( $\text{H}_2\text{SO}_4$  in the case of  $\text{Na}_2\text{SO}_4$ ) at the anode, and alkali ( $\text{NaOH}$  in the case of  $\text{Na}_2\text{SO}_4$ ) at the cathode. The anions are thus discharged from an acid solution and the cations from an alkaline solution. The degree of acidity and alkalinity are practically the same for all salts of strong acids and strong bases, and the decomposition potential is about 2.2 volts for *N*-solutions.

In the electrolysis of metal halides, hydrogen is formed by secondary decomposition at the cathode, but there is no corresponding decomposition resulting in oxygen at the anode. The decomposition voltage therefore depends upon the halide. For an *N*-solution of  $\text{NaCl}$  it is 1.98 volts.

(2) **Ionic Displacement of Hydrogen from Water.**—The action which certain metals exhibit of displacing hydrogen from water depends upon the electropositivity of the metal being greater than that of hydrogen.

When an electropositive metal is immersed in a solution of its own salt it forces some of its ions into the solution by virtue of its electrolytic solution-pressure. This process continues until the osmotic pressure produced by the additional ions equals the electrolytic dissociation pressure, leaving the metal with a negative charge which, for a given strength of solution and at a given temperature, is dependent upon the electropositiveness of the metal.

The following are the electrometric values for some of the principal elements, measured against normal solutions: Fritz Ephraim, "Inorganic Chemistry," Gurney and Jackson, 1939.

Cs . . . . .	-2.91	Cu <sup>++</sup> . . . . .	-0.29
Rb . . . . .	-2.74	Ni . . . . .	-0.22
K . . . . .	-2.61	Pb . . . . .	-0.12
Na . . . . .	-2.45	Sn . . . . .	-0.10
Ba . . . . .	-2.15	H . . . . .	0.00
Ce <sup>+++</sup> . . . . .	-2.10	Sb . . . . .	+0.1
Li . . . . .	-2.09	Bi . . . . .	+0.2
Sr . . . . .	-2.07	Ce <sup>+++</sup> . . . . .	+0.24
Ca . . . . .	-1.90	As . . . . .	+0.3
La . . . . .	-1.75	Cu <sup>+</sup> . . . . .	+0.34
Th . . . . .	-1.75	Re . . . . .	+0.6
Nd . . . . .	-1.65	Ag . . . . .	+0.80
Mg . . . . .	-1.55	Hg <sup>++</sup> . . . . .	+0.80
Pr . . . . .	-1.44	Pd . . . . .	+0.82
Al . . . . .	-1.28	Pt . . . . .	> +0.86
Mn . . . . .	-1.04	Au <sup>+</sup> . . . . .	+1.5
Be . . . . .	-0.81	Te . . . . .	-0.84
Zn . . . . .	-0.76	S . . . . .	-0.55
Ga . . . . .	< -0.76	O . . . . .	+0.39
Cr <sup>+++</sup> . . . . .	-0.6	I . . . . .	+0.54
Fe <sup>++</sup> . . . . .	-0.43	Br . . . . .	+1.08
In . . . . .	> -0.40	Cl . . . . .	+1.36
Cd . . . . .	-0.40	F . . . . .	+1.92
Tl . . . . .	-0.33		

Any of the metals above hydrogen will therefore displace it from a solution containing hydrogen ions. In the case of water where the number of hydrogen ions is low, the rate of evolution is lower than with acids, but it nevertheless does occur very readily in the cold with the alkali metals, but decreasing in extent on descending the series. The same considerations which apply to the liberation of hydrogen from water also govern its displacement from NH<sub>3</sub>.

In many cases the hydroxides formed protect the metal from further action and any method of increasing the solubility of the hydroxide, such as an increase in temperature or the application of a mass-action effect, increases the extent of the reaction.

The effect of metallic couples is to decompose water electrolytically. Metallic impurities, by forming couples, have a marked effect on the apparent readiness of a metal to replace hydrogen from water (and acids).

(3) Displacement of Hydrogen from Acids.—Hydrogen ions can be displaced as hydrogen atoms (and thence as molecules) from acid solutions similarly to their displacement from water. The greater concentration of H ions in this case, and the usually greater solubility of the salt compared with the hydroxide, facilitate the reaction. In practice it is found that the ease of displacement of hydrogen seldom

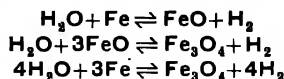
follows the series given above, since this series refers to normal solutions and the order of the metals varies with concentration. Traces of impurities also have a marked effect on the reaction for reasons which have been mentioned earlier. The reaction is facilitated by any factor which increases the number of hydrogen ions (dilution), decreases viscosity of the acid and facilitates replacement of the H ions removed from the sphere of action (increase in temperature), increases the sphere of action (powdering of the metal), or removes a protective gaseous or solid coating from the metal (dilution, etc.). Well-known examples of the inhibition of the reaction are Fe in conc. H<sub>2</sub>SO<sub>4</sub> and Pb in H<sub>2</sub>SO<sub>4</sub>, in which protective coatings of different types are formed. On exposure to an oxidising agent many metals, particularly iron, form a protective oxide coating, even when the oxidising agent is itself an acid, *e.g.* nitric, chloric, chromic. The passive metal is then insoluble even in dilute acids until another metal is introduced to set up a couple, or until the coating has been removed by reduction or other means. The salts of many weak acids are readily hydrolysed to an insoluble hydroxide or to a basic salt, so that weak acids usually have but little action on metals.

(4) Displacement of Hydrogen from Alkalis.—Many elements displace hydrogen from hydroxides, *e.g.* :

Reactants.	Products.
Na . NaOH	Na <sub>2</sub> O . . . H <sub>2</sub>
Al . NaOH	Na <sub>3</sub> AlO <sub>3</sub> . . H <sub>2</sub>
Zn . NaOH	Na <sub>2</sub> ZnO <sub>2</sub> . . H <sub>2</sub>
Sn . NaOH	Na <sub>4</sub> SnO <sub>4</sub> . . H <sub>2</sub>
B . NaOH	Na <sub>2</sub> BO <sub>3</sub> . . H <sub>2</sub>
Si . NaOH	Na <sub>4</sub> SiO <sub>4</sub> . . H <sub>2</sub>
P . NaOH	Na <sub>3</sub> PO <sub>4</sub> . . H <sub>2</sub> , PH <sub>3</sub>
Cl . NaOH	NaClO . . . HCl → NaCl

The element concerned forms part of the anion in the resulting compound and the reaction is favoured by the metal of the hydroxide being a strong cation. Thus NaOH is better than Ca(OH)<sub>2</sub>. Where possible the hydrogen combines with excess of the element so that the method applies principally to metals and those elements having metallic allotropes, *e.g.* PH<sub>3</sub>, as well as H<sub>2</sub> is formed with P, and only HCl with Cl.

(5) Reduction of Water.—The ionic displacement of H from water has already been described, but H can also be produced from water by non-ionic reaction with many metals. The reaction of water with the metals other than those at the top of the electrometric series, is probably non-ionic, *e.g.* in the high temperature reaction with Fe.



For the references to the equilibrium constants, heats and rates of these reactions, see Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1934, XIII, p. 806. The values given have since been modified (Chipman, J. Amer. Chem. Soc. 1933, 55, 3131; 1934,

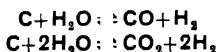
56, 2011; Emmett and Shultz, *ibid.* 1933, 55, 1376; Shibata, J. Chem. Soc. Japan, 1935, 56, 736; Tschufarov and Averbuch, Acta Physico-chim. U.R.S.S. 1936, 4, 617). When no attempt is made to discriminate between ionic and non-ionic reactions, the metals can be divided into groups according to their action on water—a concept which played an important part in early attempts to classify the metals (Thenard, "Traité de Chimie Élémentaire," Paris, 1816; Regnault, "Cours élémentaire de Chimie," Paris, 1840).

Group.	Metals.	Condition for decomposition of water.
1.	Alkali and alkaline earth.	Cold.
2.	Be, Mg, etc., and rare earths.	50–100°C.
3.	Zn, Cd, Sn, Fe, Ni, Co, Cr, Os.	Red heat, ca. 550°C.
4.	Cu, Pb, etc.	White heat, ca. 1,300°C.
5.	Hg, Ag, Au and Pt family except Os.	No reaction.

Further data, including equilibria, etc., of these reactions, have since been obtained, e.g.:

Cr, Aoyama and Kanda (J. Chem. Soc. Japan, 1934, 55, 1174). Co, Shibata and Mori (*ibid.* 1933, 54, 50; Z. anorg. Chem. 1933, 212, 305). Ni, Skapski and Dabrowski (Z. Elektrochem. 1932, 38, 365). Sn, Emmett and Shultz (J. Amer. Chem. Soc. 1933, 55, 1390); Meyer and Scheffer (Rec. trav. chim. 1935, 54, 294). Mn, Aoyama and Oka (Sci. Rep. Tôhoku, 1933, 22, 824; Amer. Chem. Abstr. 1934, 28, 1915). Metals generally, Guertler (Z. Metallk. 1926, 18, 365); Kernbaum (Compt. rend. 1911, 152, 1668); Pourbaix (Bull. Soc. Belge Ing. Ind. 1934, No. 7–8, 67 pp.). Mo, Chaudron (Compt. rend. 1920, 170, 182). Al, Scala (Atti. R. Acad. Lincei, 1913, [v], 22, i, 43; Amer. Chem. Abstr. 1913, 7, 1684). Mg, Piccardi (Gazzetta, 1930, 60, 337; Amer. Chem. Abstr. 1930, 24, 3960); Knapp (Chem. News, 1912, 105, 253); W, Chaudron (Compt. rend. 1920, 170, 1056). Ca, Lettermann (Z. physikal. Chem. Unterr. 1911, 13, 176). Zn, Schacherl (Gazzetta, 1932, 62, 839). Cu, Gallo (Annali Chim. Appl. 1937, 27, 269).

Water is also decomposed by non-metallic elements. The reaction with C is best known.

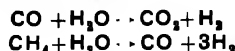


(see Chemical Reactions, p. 318a, and Gas, WATER).

Si and B act similarly. Se and Te liberate  $\text{H}_2$  from  $\text{H}_2\text{O}$ , Te more readily than Se (Montignie, Bull. Soc. chim. 1934, [v], 1, 507). S does not normally liberate  $\text{H}_2$  in its reaction with  $\text{H}_2\text{O}$ , but at 1,000°  $\text{H}_2$  begins to appear in the products (Randall and Bichowsky, J. Amer. Chem. Soc. 1918, 40, 362, 368; Lewis and Randall, "Thermodynamics," New York, 1923, p. 547). Similarly, P, under some conditions, yields  $\text{H}_2$  (Ipatiev and Freitag, Z. anorg.

Chem. 1933, 215, 388). The halogens do not liberate  $\text{H}_2$  from water.

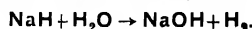
Besides the elements many compounds react with water to give  $\text{H}_2$ , e.g.:



(see Chemical Reactions, pp. 318b, 319a).

Among liquid-phase reactions in which hydrogen is produced are water with manganous oxide, uranium oxide, chromous oxide, titanous oxide, potassium cobaltocyanide, molybdenous chloride, etc. Hydrogen is sometimes evolved during the hydrolysis of some carbides ( $\text{Mn}_3\text{C}$ ) (v. Vol. II, 281c) and silicides ( $\text{CaSi}_2$ ) (v. Vol. II, 227c).

(6) Decomposition of Hydrides. —The salt-like hydrides ( $\text{NaH}$ ,  $\text{CaH}_2$ , etc.) are readily hydrolysed by water to yield hydrogen,



This reaction could also be regarded as a decomposition of water to give  $\text{H}_2$ .

The volatile hydrides behave in various ways with water. The halogen hydrides tend to ionise as acids  $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ , a tendency which appears less strongly with the VI group hydrides, e.g.  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ . The V group hydrides, such as  $\text{NH}_3$ , by virtue of the lone pair of electrons on the central atom, co-ordinate with an H of  $\text{H}_2\text{O}$  and ionise as bases,  $\text{HOH} + \text{NH}_3 \rightarrow \text{HO}^- + \text{H}^+ \text{NH}_3$ . With the IV group hydrides on the other hand the O of water tends to co-ordinate with the central atom, e.g. Si, resulting in a hydrolysis which yields  $\text{H}_2$ ,  $\text{SiH}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}_2$ . Similarly with the higher silanes. C is however unable to expand its octet and consequently  $\text{CH}_4$  is stable to  $\text{H}_2\text{O}$  at ordinary temperatures. In the III group a similar hydrolysis occurs and the boranes yield  $\text{H}_2 + \text{H}_3\text{BO}_3$ . Silane, but not methane, yields  $\text{H}_2$  with  $\text{HCl}$ ,  $\text{SiH}_4 + \text{HCl} \rightarrow \text{SiH}_3\text{Cl} + \text{H}_2$ .

Thermal decomposition of hydrides is also possible and includes all types of hydrides, e.g.  $\text{NaH}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{HBr}$ . The more important of these are dealt with either under Decomposition of Hydrocarbons (see below (7)) or Chemical Reactions, p. 319a.

(7) Decomposition of Hydrocarbons and other Organic Compounds. —Hydrocarbons readily yield hydrogen at elevated temperatures, either through rupture of the molecule into smaller fragments including  $\text{H}_2$  (cracking) or by simply splitting off  $\text{H}_2$  (dehydrogenation). These reactions are endothermic. The development of catalysis in relation to these reactions has made great progress in recent years.

In general the reactions obey certain principles:

- (i) The decomposition tends to favour the product which involves least rearrangement in the molecule.
- (ii) The C—C is more stable than the C—H link in aromatic compounds, and less stable in aliphatic compounds. This is Haber's rule and is of wide but not of universal application.
- (iii) Radicals of low electron-attraction are formed preferably to those of high electron-attraction.

See Hurd, "The Pyrolysis of Carbon Compounds," Chem. Cat. Co., 1929, Chap. II; Ellis, "The Chemistry of Petroleum Derivatives," Vol. I, Chem. Cat. Co., 1934; Vol. II, Reinhold Pub. Corp., 1937, pp. 74-76; Egloff, "The Reactions of Pure Hydrocarbons," Amer. Chem. Soc. Monograph Series, No. 73, New York, 1937, p. 187; Egloff, Levinson and Bollman, "Thermal Reactions of Aromatic Hydrocarbons," Chicago, 1934; Motovilova, "Catalytic Dehydration and Dehydrogenation of Alcohols," J. Chem. Ind. U.S.S.R., 1935, 12, 1184, 1260.

**Preparation of Pure Hydrogen.**—The preparation of small amounts of hydrogen raises completely different problems from those of industrial production. For the preparation of hydrogen on a laboratory basis the best sources of information are Gmeln, "Handbuch der anorganischen Chemie," Aufl. 8, Verlag Chemie, Berlin, 1927, System No. 2, p. 18, and Farkas and Melville, "Experimental Methods in Gas Reactions," Macmillan, New York, 1939.

The standard method is by the action of acids (dil. HCl or dil. H<sub>2</sub>SO<sub>4</sub>) on metals (Mg, Al, Zn or Fe), preferably Zn+H<sub>2</sub>SO<sub>4</sub> (diluted 1 in 8). Further details are given by Löffler (Amer. Chem. Abstr. 1927, 21, 1071) and Edwards (J. Ind. Eng. Chem. 1919, 11, 961).

The electrolysis of acids can yield reasonably pure hydrogen, e.g. 10% H<sub>2</sub>SO<sub>4</sub> with Pt electrodes set wide apart to avoid contamination by O<sub>2</sub>, followed by passage of the gas at slight pressure through alkaline pyrogallol and then water.

It is more usual, however, to electrolyse alkaline solutions, e.g. pure baryta (Baker, J.C.S. 1902, 81, 400) or 30% NaOH with pure Ni electrodes (Vézes and Labatut, Z. anorg. Chem. 1902, 32, 464; Sivkov, Amer. Chem. Abstr. 1935, 29, 53; Fink and Mantell, Trans. Electrochem. Soc. 1927, 52, 109). The procedure given by Farkas and Melville, *op. cit.*, involves purification by passing over CaCl<sub>2</sub> (to remove most of the H<sub>2</sub>O), over Pt asbestos or Pd asbestos at 300°C. (to remove O<sub>2</sub>), over P<sub>2</sub>O<sub>5</sub> and through a liquid air trap (to effect complete drying). Specially pure hydrogen is best obtained by allowing the gas to diffuse through a palladium tube into an evacuated reservoir.

Pure water may be electrolysed at 200 volts between Cu electrodes to give pure hydrogen (Saxon, Chem. News, 1931, 142, 49).

Hydrogen at pressure can be generated in a portable apparatus, depending on the ferrosilicon—NaOH reaction (Lefebvre, Chim. et Ind. 1928, 20, 231).

Hydrogen for ordinary use is conveniently purchased in cylinders at about 100 atm. pressure, or is generated in a Kipp's apparatus. In the latter case the gas contains AsH<sub>3</sub>, PH<sub>3</sub>, hydrocarbons, O<sub>2</sub> and CO<sub>2</sub> and, according to Farkas and Melville (*op. cit.*), can be purified by being passed successively through 50% KOH, saturated KMnO<sub>4</sub> twice over, CaCl<sub>2</sub>, over Pt asbestos at 800°C. in a silica tube, CaCl<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>. A more detailed account of individual impurities and their method of removal is given in Gmeln, "Handbuch der anorganischen Chemie," Aufl. 8, 1927. Pure hydrogen may also be obtained

by evaporation from liquid hydrogen (U.S.P. 2022165).

When drying is effected either by passing the gas over drying agents or through cooled traps, the weight of H<sub>2</sub>O in grams per cubic metre remaining when the systems are in equilibrium

#### Cold traps:

−193°C. . . . .	0.7 × 10 <sup>−23</sup>
−115°C. . . . .	2.4 × 10 <sup>−4</sup>

#### Drying agents (at 25°C.):

P <sub>2</sub> O <sub>5</sub> . . . . .	< 2 × 10 <sup>−5</sup>
Mg(ClO <sub>4</sub> ) <sub>2</sub> . . . . .	< 5 × 10 <sup>−4</sup>
Mg(ClO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O . . . . .	2 × 10 <sup>−3</sup>
KOH (fused) . . . . .	2 × 10 <sup>−3</sup>
Al <sub>2</sub> O <sub>3</sub> . . . . .	3 × 10 <sup>−3</sup>
H <sub>2</sub> SO <sub>4</sub> . . . . .	3 × 10 <sup>−3</sup>
CaCl <sub>2</sub> . . . . .	2.5 × 10 <sup>−1</sup>

**Estimation of Hydrogen.**—On passing a gas containing hydrogen slowly over palladised asbestos heated to dull redness, hydrogen is removed completely, leaving paraffins unaffected. CO, CO<sub>2</sub>, H<sub>2</sub>O, benzene, alcohol, HCl or NH<sub>3</sub> interfere. Hg destroys the activity of the Pd. See Lunge and Ambler, "Technical Gas Analysis," Gurney and Jackson, 1934.

#### PHYSICAL PROPERTIES.

Unless otherwise specified, the following data refer to molecular hydrogen containing the naturally existing ratio of protium and deuterium atoms (about 5,000 to 1), the molecules being normal in respect to ortho and para, i.e. 0.7492 ortho and 0.2508 para.

**Atomic Weight.**—H on the physical scale is 1.0081, on the chemical scale this becomes 1.00785; allowance for <sup>2</sup>H with the abundance ratio 1:5000 gives 1.00805 for chemical hydrogen, and 1.0081 has been adopted (Eighth Report of the Committee on Atomic Weights of the International Union of Chemistry, in Baxter, Honigschmid and LeBeau, J. Amer. Chem. Soc. 1938, 60, 737). A complete review on the atomic weight of hydrogen is given by Brescia and Rosenthal (J. Chem. Educ. 1939, 16, 491).

**Pressure/Temperature/Volume Relationships, etc.**—(See table on opposite page.)

The figure for 1 atm. 0°C. is taken from Blanchard and Pickering (U.S. Bureau of Standards Sci. Paper, No. 529, 1926). The remainder are from Deming and Shupe (Physical Rev. 1932, [ii], 40, 848).

The equation of state put forward by Beattie and Bridgeman (J. Amer. Chem. Soc. 1928, 50, 3133; Proc. Amer. Acad. Arts. Sci. 1928, 63, 229) is applicable over a wide range of temperature and pressure. The equation is

$$p = [RT(1 - \epsilon)/V^2] \times [V + B] - A/V^2$$

Mol. wt. adopted 2.0154.

Where

$$A = A_0 [1 - (a/V)]$$

$$B = B_0 [1 - (b/V)]$$

$$\epsilon = c/VT^3$$

$$R = 0.08206$$

$$V = \text{litres per g.-mol.}$$

$$p = \text{atmospheres}$$

$$T = ^\circ\text{K} = ^\circ\text{C} + 273.13^\circ$$

$p$ .	$v$ .	$d$ .	$f$ .	$-\frac{p}{v} \left( \frac{dv}{dp} \right)_T$	$\frac{T}{v} \left( \frac{dv}{dT} \right)_p$
$t = -50^\circ\text{C}.$					
25	744.7	2.707	25.41	0.983	0.9956
100	196.3	10.27	107.1	0.927	0.9695
1,000	34.10	59.11	2,252	0.524	0.5592
$t = 0^\circ\text{C}.$					
1		0.08988			
25	910.3	2.214	25.38	0.985	0.9917
100	238.6	8.447	106.4	0.936	0.9617
1,000	38.35	52.50	1,993	0.586	0.6026
$t = 100^\circ\text{C}.$					
25	1,240	1.625	25.31	0.988	0.9905
100	322.0	6.259	105.2	0.949	0.9614
1,000	46.75	43.12	1,696	0.671	0.6676
$t = 500^\circ\text{C}.$					
25	2,554	0.7891	25.16	0.993	0.9938
100	651.7	3.093	102.7	0.972	0.9753
1,000	79.91	25.22	1,312	0.814	0.7987

$p$  = pressure in atmospheres.  
 $v$  = volume in cubic centimetres per g.-mol.  
 $d$  = density in grams per litre.  
 $f$  = fugacity in atmospheres.

$-\frac{p}{v} \left( \frac{dv}{dp} \right)_T$  = coefficient of expansion with pressure.  
 $\frac{T}{v} \left( \frac{dv}{dT} \right)_p$  = coefficient of expansion with temperature.

and for  $\text{H}_2$   $A_0 = 0.1975$   
 $a = -0.00506$   
 $B_0 = 0.02096$   
 $b = -0.04359$   
 $c = 0.0504 \times 10^4$

For the compression of mixtures the compressibility of each actual mixture is required. The compressibility of binary mixtures of hydrogen is treated in general terms by Kleeman (J. Franklin Inst. 1930, 209, 229). Mixtures suitable for ammonia synthesis have been examined over a very wide range of temperature and pressure (Bartlett, J. Amer. Chem. Soc. 1927, 49, 1955; 1928, 50, 1275; Deming and Shupe, *ibid.* 1930, 52, 1382).

**Specific Heat.** Probably the best values for the specific heat of hydrogen gas at  $15^\circ\text{C}$  are:

$c_p$ (cal. per g.)	3.40
$c_p$ (cal. per g.-mol.)	6.86
$c_v$ (cal. per g.)	2.41
$c_v$ (cal. per g.-mol.)	4.87
$\gamma$	1.41

The variation of  $C_p$  with temperature is given to within 1% of the theoretical by the expression:

$C_p$  (cal. per g. mol.)  
 $= 6.88 + 0.000066T + 0.000000279T^2$   
 (Bryant, Ind. Eng. Chem. 1933, 25, 820).  
 Similarly the variation of  $C_v$  is given by

$C_v$  (cal. per g. mol.)  
 $= 4.87 + 0.000539T + 0.000000146T^2$ .

(Kemble and Van Vleck, Physical Rev. 1923, [ii], 21, 653). - See also Schuster (Wärme, 1935, 58, 39); Gumz (Feuerungstech. 1935, 23, 85);

Chipman and Fontana (J. Amer. Chem. Soc. 1935, 57, 48); Spencer and Justice (*ibid.* 1934, 56, 2311); for high temperatures and pressures, Gelperin and Rips (Khimstroj, 1934, 6, 455); for high temperatures, Bruckner (Z. anal. Chem. 1935, 100, 281) and David and Leah (Phil. Mag. 1934, [vii], 18, 307); for high pressures, Godnev and Sverdlin (Khimstroj, 1934, 6, 8); for low temperatures and high pressure, Gelperin and Rips (*ibid.* 1934, 6, 509); for quantum theory and specific heat, Van Vleck (Physical Rev. 1926, [ii], 23, 980); for  $C_p/C_v$  ratio, Workman (*ibid.* 1931, [iii], 37, 1345); and for total heat content, Lewis and Elbe (J. Amer. Chem. Soc. 1935, 57, 612), De Witt (Chem. Met. Eng. 1935, 42, 333) and Taylor (Ind. Eng. Chem. 1934, 26, 470). See also Partington and Shilling, "The Specific Heats of Gases," Benn Ltd., 1924.

**Thermal Conductivity.**—The best value of  $kT$  at  $0.0^\circ\text{C}$ . is claimed to be  $414 \times 10^{-6}$  g.-cal. per cm. per  $1^\circ$  per sec. There is, however, a certain amount of variation in reported values at  $0.0^\circ$ .

$423.8 \times 10^{-6}$	(Weber, Ann. Physik. 1927, [iv], 82, 479.)
406.0	.. (Hercus and Laby, Phil. Mag. 1927, [vii], 3, 1061.)
413.0	.. (Kannuluik and Martin, Proc. Roy. Soc. 1934, A, 144, 496.)
414.0	.. (Ulsamer, Z. Ver. deut. Ing. 1936, 80, 537.)
$424.5 \pm 2.9$ $\times 10^{-6}$	(Nothdurft, Ann. Physik. 1937, [v], 28, 137.)

Critical surveys are given by Ulsamer and also by Trautz and Zündel (Z. tech. Phys. 1931, 12, 273).

The temperature coefficient is given by  $kT = AT^n$  where  $A$  and  $n$  are constants. The value at  $295.1^\circ\text{K}$  is  $459.0 \times 10^{-6}$  and at  $593.4^\circ\text{K}$  is  $708.0 \times 10^{-6}$ .

Mixtures of industrially important gases are considered by Ibbs and Hirst (Proc. Roy. Soc. 1929, A, 123, 134).

Entropy.—Values in g.-cal. per mol. per degree:

	$-50^\circ\text{C.}$	$0^\circ\text{C.}$	$100^\circ\text{C.}$	$500^\circ\text{C.}$
1 atm.	29.265	30.648	32.843	37.903
25 "	22.84	24.24	26.44	31.50
100 "	20.01	21.44	23.66	28.74
1,000 "	15.14	16.67	18.97	24.13

(Deming and Deming, Physical Rev. 1934, [ii], 45, 109).

Solubility.—The solubility of  $\text{H}_2$  in water obeys Henry's law fairly closely at moderate temperatures and pressures. The values at 1 atm. pressure in c.c.  $\text{H}_2$  ( $0^\circ\text{C.}$ , 760 mm.) per c.c. water are:

$0^\circ\text{C.}$	$10^\circ\text{C.}$	$20^\circ\text{C.}$	$50^\circ\text{C.}$	$100^\circ\text{C.}$
0.02148	0.01955	0.01819	0.01608	0.0160

(Winkler, Ber. 1891, 24, 89; Landolt-Bornstein, "Tabellen," 1923, 1, 763).

At higher pressures c.c.  $\text{H}_2$  ( $0^\circ\text{C.}$ , 760 mm.) per g. water are:

Pressure (atm.)	$0^\circ\text{C.}$	$10^\circ\text{C.}$	$20^\circ\text{C.}$	$50^\circ\text{C.}$	$100^\circ\text{C.}$
25	0.5363	0.4870	0.4498	0.4067	0.4615
100	2.130	1.932	1.785	1.612	1.805
1,000	18.001	16.623	15.592	14.404	15.775

(Wiebe and Gaddy, J. Amer. Chem. Soc., 1934, 56, 76).

For solubility of  $\text{H}_2$  in liquid ammonia, see Wiebe and Tremearne, *ibid.* 1934, 56, 2357; for  $\text{H}_2$  and  $\text{N}_2$  in water at  $25^\circ$ , see Wiebe and Gaddy, *ibid.* 1935, 57, 1487; for  $\text{H}_2$  in individual hydrocarbons, see Ipatiev and Levin, J. Phys. Chem. U.S.S.R. 1935, 6, 632; for  $\text{H}_2$  in other organic solvents, see Frolich, Tauch, Hogan and Peer, Ind. Eng. Chem. 1931, 23, 648, and Maxted and Moon, Trans. Faraday Soc. 1936, 32, 769.

Dielectric Constant.—At  $0^\circ\text{C.}/1$  atm. the dielectric constant is 1.0002697 (Michels, Sanders and Schipper, Physica, 1935, 2, 753).

Spectrum.—The spectrum of hydrogen exhibits four prominent lines:  $\text{H}\alpha$  6562A (red),  $\text{H}\beta$  4861A (greenish-blue),  $\text{H}\gamma$  4340A (blue) and  $\text{H}\delta$  4102A (indigo). The hydrogen spectrum is one of the most complicated of all, and for further details and discussion, see Richardson, "Molecular Hydrogen and Its Spectrum," Yale University Press, 1934; Sommerfeld, "Atomic Structure and Spectral Lines," Dutton & Co. 1935; Kronig, "Band Spectra and Molecular Structure," Macmillan Co., 1930; Jevons, "Band Spectra of Diatomic Mole-

cules," Cambridge University Press, 1932; White, "Introduction to Atomic Spectra," New York, 1934; Condon and Shortley, "Theory of Atomic Spectra," Cambridge University Press, 1935; Tolansky, "Fine Structure in Line Spectra and Nuclear Spin," Methuen, 1935; Herzberg, "Atomic Spectra and Atomic Structure," translated by Spinks, New York, 1935; "Molekülspektren und Molekülstruktur," Bd. I, Dresden, 1939.

Adsorption.—The development, particularly over the last two decades, of many catalytic processes in which hydrogen is employed, has given considerable impetus to the study of catalysis and has led, in its turn, to the close study of the adsorption of hydrogen and other gases on the various substances used as catalysts. The substances which have received most attention are metals such as copper and nickel, metal oxides such as those of zinc, chromium, manganese, together with such well-known general adsorbents as charcoal and silica gel. Developments in this field are summarised in Faraday Society Discussion, Trans. Faraday Soc. 1919, 14, 173; 1932, 28, 129, by Wansbrough-Jones (Science Progress, 1932, 26, 398) and Gregg ("Adsorption of Gases by Solids," Methuen & Co., 1934).

The existence of at least two quite different types of adsorption has been shown by various investigators. Benton and White (J. Amer. Chem. Soc. 1930, 52, 2325), in a study of the adsorption of hydrogen on copper and nickel, found that adsorption at low temperatures (below  $-190^\circ\text{C.}$ ) is small but rapid, involving a small heat of adsorption; above  $-190^\circ\text{C.}$ , with a maximum at  $-100^\circ\text{C.}$ , the amounts adsorbed are greater, with a high heat of adsorption.

Similar results were obtained by Garner and Kingman (Nature, 1930, 126, 352) for hydrogen and carbon monoxide on zinc-chromium oxides; by Taylor and Williamson (J. Amer. Chem. Soc. 1931, 53, 2168) for hydrogen on manganese oxides and manganese-chromium oxides; and by Taylor and Sickman (*ibid.* 1932, 54, 602) of hydrogen on zinc oxide.

The concept of *activated adsorption* was introduced by Taylor (*ibid.* 1930, 52, 5298; 1931, 53, 578) to differentiate the high temperature, high-energy type of adsorption from the "molecular" or "Van der Waals" type which occurs at lower temperatures and with small energy changes. Various other names have been suggested—"chemical," "primary," or "activated" adsorption as against "physical," "secondary," or "molecular" adsorption—but in general the conception is the same.

"Activated" adsorption proceeds with a measurable velocity, as if a considerable energy of activation is required. As shown by Benton and White, for hydrogen on copper and nickel it begins around liquid-air temperatures; with zinc oxide, manganous oxide or their mixtures with chromium oxide, it becomes measurable between  $0^\circ$  and  $100^\circ$ , whilst with alumina and glass it does not appear until  $400^\circ$ . With charcoal, temperatures of  $400$ – $530^\circ$  are required (Kingman, Trans. Faraday Soc. 1932, 28, 269). In all cases, the heat of adsorption lies within the limits 10–30 kg.-cal. per g.-mol.  $\text{H}_2$  adsorbed.



"Molecular" adsorption on metal or oxide surfaces shows heats of adsorption of lower order, 1-2 kg.-cal. per g.-mol. These are in close agreement with the values obtained for adsorbents such as charcoal, silica, etc.

"Activated" and "molecular" adsorption overlap to a considerable extent, particularly at medium temperatures, adsorption isotherms being normally compounded of two superimposed isotherms corresponding to the two different types of adsorption.

A close correlation is found between adsorption of hydrogen on catalysts such as those cited above and the activities of these catalysts in hydrogenation reactions. Mixed zinc-chromium oxides, for example, adsorb considerably greater quantities of hydrogen than either oxide alone, while the mixed oxides are well known as more active catalysts than the separate components for the synthesis of methanol (*v. Vol. II, 350a, 425c*).

From experiments over a wide range of temperature Benton (*ibid.* 1932, 28, 202) considers that three different processes occur, physical adsorption, activated adsorption and probably solubility. Ward (*ibid.* 1932, 28, 399) is of the opinion that solution alone is sufficient to account for all the observed facts.

Palladium "occludes" hydrogen so much more strongly than any other metal that earlier researches on the phenomenon were devoted almost entirely to palladium and in particular to the precise nature of the substance or substances formed after occlusion is complete. Though there is still some uncertainty, considerable evidence has been accumulated indicating that the adsorbed hydrogen is in the atomic form. The equation of Sieverts, according to which adsorption at low pressures is practically proportional to the square root of the pressure, is usually explained by the assumption that hydrogen is in the atomic form. Some objections have been raised to this interpretation (*cf.* Ward, *Proc. Roy. Soc.* 1931, A, 133, 531; Tammann, *Z. anorg. Chem.* 1930, 188, 396). But the strong effect of occlusion of hydrogen on the electronic properties of palladium, such as electrical resistance, magnetic susceptibility, colour, photo-electric sensitivity and the thermoe.m.f. against alloys of palladium with silver and gold, all tend to the conclusion that the adsorbed hydrogen is atomic (*cf.* Coehn and Specht, *Z. Physik*, 1930, 62, 1).

The fact that, while palladium adsorbs hydrogen with ease during electrolysis, adsorption in the gas phase depends very considerably on the previous history of the metal, is now explained by the assumption that hydrogen can only enter the metal lattice as atoms. In electrolysis hydrogen atoms are produced directly; in adsorption from the gas phase the molecules must first dissociate on the adsorbing surface, and according as the surface is more or less poisoned, so will its catalytic activity in the reaction  $H_2 \rightarrow 2H$  be less or greater. Evidence has been brought forward by Smith and Dergo (*Trans. Electrochem. Soc.* 1934, 66, 25) that occlusion occurs in the intergranular fissures, rather than on the grain faces.

The heat of occlusion is about 9 kg.-cal. per

g.-mol.  $H_2$  (Gillespie and Hall, *J. Amer. Chem. Soc.* 1926, 48, 1207).

**Liquid Hydrogen.**—The boiling-point of hydrogen is 20.37°K. (*i.e.* -252.81°C.) at 1 atm. (Blue and Hicks, *J. Amer. Chem. Soc.* 1937, 59, 1962). The molecular heat of vapourisation =  $219.7 - 0.27(T - 16.6)^2$  g.-cal. per g.-mol. (Simon and Lange, *Z. Physik*, 1923, 15, 312). The vapour pressure of liquid hydrogen is given by

$$\log p_{H_2} \text{ (mm.)} = -37.7882(1/T) + 1.75 \log T + 0.0023127T + 2.39078$$

(Henning, *ibid.* 1927, 40, 775; Henning and Otto, *Physikal. Z.* 1936, 37, 633). The molar heat capacity of liquid hydrogen is  $0.33 + 0.206T$  (Simon and Lange, *l.c.*).

The density of the liquid

$$= 0.084404 - 223 \times 10^{-6} T_K - 21.83 \times 10^{-6} T_K^2.$$

(*Int. Crit. Tables*), *i.e.* 0.07085 at the boiling-point, and 0.07709 at the triple point.

Liquefaction of hydrogen is worked on the Lande principle (*see below*), and liquid hydrogen has been increasingly used recently in research work. Simple forms of apparatus for its preparation are described by Ruhemann (*Z. Physik*, 1930, 65, 67), Keyes, Gerry and Hicks (*J. Amer. Chem. Soc.* 1937, 59, 1426) and Ahlberg, Estermann and Lundberg (*Rev. Sci. Instr.* 1937, 8, 422).

**Solid Hydrogen.**—The melting-point of hydrogen is 14.13°K. (Henning, *Z. Physik*, 1927, 40, 775). The triple point is 13.94°K. (Blue and Hicks, *J. Amer. Chem. Soc.* 1937, 59, 1962). The critical data are: temperature 33.25°K., pressure 12.80 atm., density 0.3102 g. per c.c. (Woolsey, *ibid.* 1937, 59, 1577).

Solid hydrogen has a density of  $0.0890 \pm 0.0004$  at 4.2°K. (Megaw and Simon, *Nature*, 1936, 138, 242; Megaw, *Phil. Mag.* 1939, [vii], 28, 129); 0.08077 at 11.2°K. and 0.0763 at 13.3°K. (*Int. Crit. Tables*).

Solid hydrogen is formed by pumping off liquid hydrogen.

#### CHEMICAL REACTIONS.

The heats of reaction given refer to kilogram cal. (15°C.) per g. mol. at 0°C., 1 atm. pressure; a positive sign is given to values of  $\Delta H$  and  $\Delta F$  to represent endothermic reactions and a negative sign to represent exothermic reactions.

**Dissociation.**—At high temperatures  $H_2$  dissociates into atoms:

$$\log_{10} K = -\frac{21,200}{T} + 1.765 \log_{10} T - 9.85 \times 10^{-5} T - 0.256, \text{ e.g. :}$$

The degree of dissociation at 1 atm. is:

$$\begin{aligned} &2.56 \times 10^{-34} \text{ at } 300^\circ\text{K.} \\ &1.22 \times 10^{-3} \text{ at } 2,000^\circ\text{K.} \\ &0.0469 \text{ at } 5,000^\circ\text{K.} \\ &0.9996 \text{ at } 10,000^\circ\text{K.} \end{aligned}$$

(Langmuir, *J. Amer. Chem. Soc.* 1912, 34, 1310; 1914, 36, 1708; 1915, 37, 417; 1916, 38, 1145; *Ind. Eng. Chem.* 1927, 19, 667).

The heat of dissociation is 102.72 according to

Beutler (Z. physikal. Chem. 1935, B, 29, 315), and 103-680 according to Poole (Proc. Roy. Soc. 1937, A, 163, 404). The reaction is endothermic.

The following free energy equation was provisionally put forward by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Co., 1923, p. 471.

$$\Delta F = 81,000 - 3.5T \log T + 0.00045T^2 + 1.17T.$$

A more recent expression is given by E. N. Jeremin (Acta Physicochim. U.R.S.S. 1935, 3, 147),

$$\Delta F = 102,000 - 7.185T \log T + 0.000033T^2 + 0.000000465T^3 - 2.332T$$

**Halogens.**—The affinity of hydrogen for the halogens decreases on passing from F to I, as indicated by the following data.

*Heats of Formation:*

**HF(g.)**  $\Delta H = -64.45$  Von Wartenburg and Schütze (Z. anorg. Chem. 1932, 206, 65).

**HCl(g.)**  $\Delta H = -22.0$  International Critical Tables.

**HBr(g.)**  $\Delta H = -8.5$  Ditto.

**HI(g.)**  $\Delta H = +6.0$  Ditto.

*Equilibrium Constants.*— $2\text{HX} \rightleftharpoons \text{H}_2 + \text{X}_2$ .

$\text{X} = \text{Cl}$ ,  $\log K_p = (-9586/T) + 0.440 \log T - 2.16$  (Wohl and Kadow, Z. physikal. Chem. 1925, 118, 460).

$\text{X} = \text{Br}$ ,  $\log K_p = (-5223/T) + 0.553 \log T - 2.72$  (Nernst, Z. Elektrochem. 1909, 15, 691).

$\text{X} = \text{I}$ ,  $\log K_p = (-540.4/T) + 0.503 \log T - 2.35$  (Von Falckenstein, Z. physikal. Chem. 1910, 68, 270; 72, 113).

The heats of activation of the reactions  $\text{X} + \text{H}_2$  and  $\text{H} + \text{X}_2$  are as follows:

$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \dots$	6.0
$\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H} \dots$	17.7
$\text{I} + \text{H}_2 \rightarrow \text{HI} + \text{H} \dots$	33.0
$\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \dots$	3.0
$\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br} \dots$	1.0
$\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I} \dots$	0

(Morris and Pease, J. Chem. Phys., 1935, 3, 796), and for the reactions  $\text{X}_2 + \text{H}_2$ :

$\text{Br}_2 + \text{H}_2 \dots$	40
----------------------------------	----

(Semenoff, "Chemical Kinetics and Chain Reactions," Clarendon Press, Oxford, 1935, p. 140),

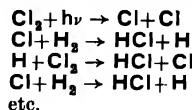
$\text{I}_2 + \text{H}_2 \dots$	40
---------------------------------	----

(Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, Oxford 1933, p. 79).

Hydrogen and fluorine combine explosively under all conditions, even in the dark at  $-252^\circ\text{C}$ . Hydrogen and chlorine readily combine (explosively under some conditions), either light or heat inducing the reaction. Both the thermal and photochemical reactions are also known for hydrogen and bromine (explosive under some conditions). In the reaction between hydrogen and iodine, only the thermal reaction has been observed.

The reaction between hydrogen and chlorine has received exhaustive study, and has played

very important role in the development of the theory of chain reactions. According to Nernst the reaction proceeds through the absorption of quantum of light by the  $\text{Cl}_2$  molecule:



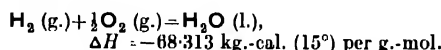
The reaction is provoked by light or heat; there may be a long induction period, due to the formation of  $\text{NCl}_3$  (from nitrogenous impurities) and persisting until this inhibitor disappears; the quantum yield is very high (up to  $10^5$  molecules  $\text{HCl}$  per quantum of light); traces of moisture are claimed to be essential. The relationships of rate with light intensity,  $\text{Cl}_2$ ,  $\text{H}_2$  and  $\text{O}_2$  pressures are given by the formula:

$$\frac{d[\text{HCl}]}{dt} = \frac{2k_3 I [\text{Cl}_2] [\text{H}_2]}{[\text{O}_2] (k_4 [\text{H}_2] + k_5 [\text{Cl}_2])}$$

$I$  = intensity of the light.

See Semenoff (*op. cit.*) and Hinshelwood (*op. cit.*).  $\text{H}_2 + \text{F}_2$ , Eyring and Kassel (J. Amer. Chem. Soc. 1933, 55, 2976); Bodenstein and Jockusch (Sitzungsber. Preuss. Akad. Wiss. Berlin, Phys. Math. Klasse, 1934, 27; Amer. Chem. Abstr. 1934, 28, 2978).  $\text{H}_2 + \text{Cl}_2$ , Semenov (J. Phys. Chem. U.S.S.R., 1933, 4, 4); Zotsky and Günther (Z. physikal. Chem. 1934, B, 26, 373); Griffiths and Norrish (Proc. Roy. Soc. 1934, A, 147, 140).  $\text{H}_2 + \text{Br}_2$  and  $\text{H}_2 + \text{I}_2$ , Bodenstein (Helv. Chim. Acta, 1935, 18, 743).

**Oxygen.**—The heat of formation of water measured at  $25^\circ$  and at a constant pressure of 1 atm. is:



(Rossini, Bur. Stand. J. Res. 1931, 6, 1; Proc. Nat. Acad. Sci. 1930, 16, 694).

Taking  $\text{H}_2\text{O}(\text{l.}) = \text{H}_2\text{O}(\text{g.})$ ,

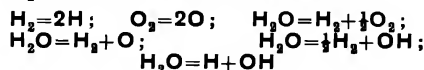
$\Delta H = +9.721 \text{ kg.-cal. } (15^\circ) \text{ per g.-mol. (Intern. Crit. Tables); } \text{H}_2(\text{g.}) + \frac{1}{2}\text{O}_2(\text{g.}) = \text{H}_2\text{O}(\text{g.}),$   
 $\Delta H = -57.592 \text{ kg.-cal. } (15^\circ) \text{ per g.-mol.}$

The equilibrium for  $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$ , is given by

$$\log K_c = (-24900/T) + 1.335 \log T - 9.65 \times 10^{-5}T + 1.37 \times 10^{-7}T^2 - 6.65 \times 10^{-11}T^3 - 1.08$$

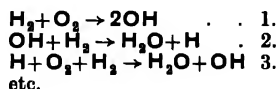
(Siegel, Z. physikal. Chem. 1914, 87, 659).

Equilibrium constants for the reactions:



are given by Zeise (Z. Elektrochem. 1937, 43, 704).

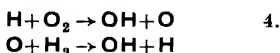
According to Haber's view the reaction proceeds:



Hinshelwood proposed the initial formation of  $\text{H}_2\text{O}_2$ . Owing to the equilibrium  $\text{H}_2\text{O}_2 \rightleftharpoons 2\text{OH}$ , the views may not be irreconcilable.

At temperatures below about  $550^\circ\text{C}$ . the rate of reaction is moderately slow and bears no unusual relationship to pressure. Above this temperature, however, the rate of combination of a given mixture of  $\text{H}_2$  and  $\text{O}_2$  increases gradually with pressure exhibiting a regular curve, until a pressure is reached at which the reaction proceeds explosively. The explosive reaction occurs over a certain range of pressure, above which the slow reaction reappears and proceeds, with increase in pressure, at rates which are a continuation of the interrupted curve. Finally the rate reaches a value comparable with the rate of the explosive reaction.

The explosion is due to the fact that, whereas normally the reaction proceeds according to the chain, branching occurs in the explosive reaction, in particular:



Thus both products of the first branching (4) are capable of giving rise to fresh chains.

The probability of the branching reaction occurring is given by

$$\delta = \frac{2.5 \times 10^5 e^{-U/RT}}{[\text{H}_2]}$$

where  $U$  is the energy of activation of reaction (4) and is equal to about 27.8 (Semenoff, *l.c.* See also Kontorova and Nalbandyan, *Physikal. Z. Sovietunion*, 1933, 4, 758).

The lower pressure limit of explosion is determined by the de-activation of the chains at the surface of the vessel; the upper limit by the de-activation in the gas phase (*v. EXPLOSIONS, GASEOUS*).

At  $550^\circ\text{C}$ . the lower explosive limit is a few mm. pressure, whilst the upper limit is about 100 mm.

These limits vary according to many factors. The lower limit, immediately above the minimum temperature, is decreased by rise in temperature, but subsequently remains independent of temperature. The upper limit is increased regularly by increase in temperature.

Ratios of  $\text{H}_2/\text{O}_2$  far removed from 2:1 narrow the explosive ranges. The optimum ratio requires the oxygen to be in slight excess (Mitscherlich, *Z. anorg. Chem.* 1916, 98, 145).

Inert gases tend to buffer the chains in their approach to the walls where they would be de-activated. They thus lower the lower limit and also somewhat lower the upper limit.

A decrease in the size of vessel raises the lower limit but is without effect on the upper limit.

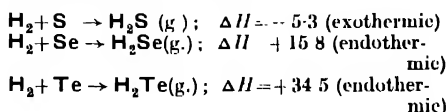
The halogens lower both limits and if present in sufficient quantity prevent the explosion altogether (Hinshelwood and Garstang, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 656). Trichloroethylene, tin tetramethyl, dimethyl selenide and telluride and ethyl bromide can also be used to suppress the reaction (Tanaka and Nagai, *Proc. Imp. Acad. Tokyo*, 1929, 5, 80, 418, 422, etc.).

The limits of inflammability of  $\text{H}_2$  are given in the U.S. Dept. Int. Bulletin 279:

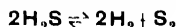
	Lower.	Upper.
$\text{H}_2$ in $\text{O}_2$	4%	94%
$\text{H}_2$ in air.	4%	74%

**Bibliography.**—Hinshelwood, "Kinetics of Chemical Change," Oxford, Clarendon Press, 1940; Hinshelwood and Williamson, "The Reaction between Hydrogen and Oxygen," Clarendon Press, Oxford, 1934; Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Clarendon Press, 1935.

**Sulphur, Selenium, Tellurium.**—Combination with  $\text{H}_2$  takes place less readily on passing from S to Te. The heats of reaction (International Critical Tables) are:



The equilibrium for the reaction



is:

$^\circ\text{C}.$	750	830	945	1,065	1,132
$K_p \times 10^4$	0.89	3.8	24.5	118	200

(Preuner and Schupp, *Z. physikal. Chem.* 1909, 73, 157).

The heat of activation is about 43 kg.-cal.

The kinetics of the reaction have been studied by Cook and Robinson (*J.C.S.* 1936, 454). See also Jones and Sherman (*J. Chem. Physics*, 1937, 5, 375).

**Nitrogen.**—The direct reaction between  $\text{H}_2$  and  $\text{N}_2$  is of immense industrial importance (*v. AMMONIA*, Vol. I, pp. 332–338).

For the reaction  $2\text{NH}_3 \rightleftharpoons 3\text{H}_2 + \text{N}_2$ ,

$$\log K_p = (2098.2/T) - 2.509 \log T - 1.006 \times 10^{-4} T + 1.859 \times 10^{-7} T^2 + 2.10$$

(Haber, *Z. Elektrochem.* 1914, 20, 603). For high pressures the values determined by Larson (*J. Amer. Chem.* 1924, 46, 367) are more accurate.

The heat of the reaction is given by the equation:



(Haber, Tamaru and Oehlm, *Z. Elektrochem.* 1915, 21, 206); for the heat of reaction at higher temperatures, see Haber and Tamaru (*ibid.* p. 191).

The heat of activation of the homogeneous reaction is extremely high and only the heterogeneous reaction is important for the formation of  $\text{NH}_3$ , in which case the heat of activation depends upon the particular catalyst.

The best catalysts are reduced Fe promoted by oxides such as  $\text{Al}_2\text{O}_3$ , in addition to  $\text{K}_2\text{O}$  (Larson, *Ind. Eng. Chem.* 1924, 16, 1002). S and O compounds poison the catalyst.

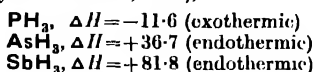
The reaction probably proceeds through the following mechanism: (i)  $\text{N}_2$  is adsorbed on the catalyst and is activated or even dissociated, (ii)  $\text{H}_2$  is similarly adsorbed and forms  $\text{NH}$  with the N, (iii)  $\text{NH}$  is reduced by molecular  $\text{H}_2$  to  $\text{NH}_3$  (Frankenburger, *Z. Elektrochem.* 1933, 39, 45, 97, 269).

Since the mechanism is incompletely understood, no kinetic expression is entirely satisfactory but the arbitrary formula of Benton (Ind. Eng. Chem. 1927, **19**, 494) agrees with the experimental data over a wide range,

$$\frac{X}{t} = \frac{3P^2k_1S}{16apnH_3}$$

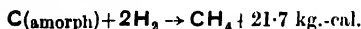
- X = volume fraction of  $NH_3$  formed.  
 t = time of passage over catalyst.  
 P = total pressure.  
 $k_1$  = velocity constant of synthesis reaction.  
 S = constant depending on catalyst.  
 a = constant depending on temperature.  
 $p_{NH_3}$  = partial pressure of  $NH_3$ .

**Phosphorus, etc.**—Nascent hydrogen reacts with the elements to give  $PH_3$ ,  $AsH_3$ ,  $SbH_3$  and  $BiH_3$  as well as lower hydrides. The heat of formation (Ephraim, "Inorganic Chemistry," Gurney and Jackson, 1939),



indicate the usual decrease in affinity on passing down the group.

**Carbon.**—Pure carbon does not react readily with  $H_2$ , but at high temperatures, especially if catalysed by Co or Ni, reaction occurs to an appreciable extent



(see Riley, Phil. Mag. 1924, [vi], **48**, 126).

The equilibrium constant  $K = [CH_4]/[H_2]^2$  may be calculated from the data of Pring and Fairlie (J.C.S. 1912, **101**, 91).

T (° absolute):

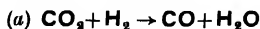
823	1,473	1,548	1,573	1,648
-----	-------	-------	-------	-------

K:

0.64	0.00244	0.00147	0.00146	0.00100
------	---------	---------	---------	---------

This equilibrium is discussed fully by Gordon and Barnes (J. Physical. Chem. 1932, **36**, 2601).

**Carbon Dioxide.**—

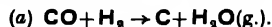


$\Delta H = +10.1$  (endothermic).

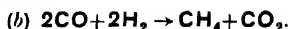
$K_p: \log K_p = (-2150/T) - 1.8 \times 10^{-7}T^2 + 2.2$  (Neumann and Kohler, Z. Elektrochem. 1928, **34**, 218; also Scheibel, Monatsh. 1931, **58**, 183; Kassel, J. Amer. Chem. Soc. 1934, **56**, 1838; see also GAS, WATER).



**Carbon Monoxide.**—Carbon monoxide and hydrogen react under varying conditions of concentration, pressure, temperature, catalyst and purity to give a great variety of products, many of which are of the greatest importance. The following are known reactions, though not necessarily representing the reaction mechanism:



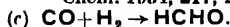
$\Delta H: -31.4$  (exothermic). The reverse of this reaction is, of course, the basis of water-gas production (v. GAS, WATER).



$\Delta H: -61.8$  (exothermic).

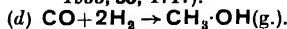
$\Delta F: -56,950 + 15.075T \ln T - 0.01078T^2 + 0.00000031T^3 - 30.34T$  (D. F. Smith, Ind. Eng. Chem. 1927, **19**, 801).

$K_p: 1/\log K_p = (-57,903/4.573T) + 13.875$  (Fischer and Pichler, Brennstoff-Chem., 1931, **12**, 365; Schmidt and Neumann, Z. Elektrochem. 1932, **38**, 926; Ghosh, Chakravarty and Bakshi; Z. anorg. Chem. 1934, **217**, 277).



$\Delta H: -2.0$  (exothermic).

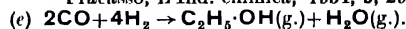
$K_p: \log K_p = (1,710/4.573T) - 5.431$  (Newton and Dodge, J. Amer. Chem. Soc. 1933, **55**, 4747).



$\Delta H: -33.6$  (exothermic).

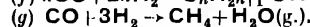
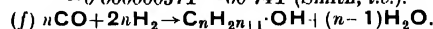
$\Delta F: -20,857 + 17.88T \ln T - 0.01423T^2 - 64.04T$  (Smith, l.c.).

$K_p: \log K_p = (17,030/4.573T) - 9.1293 \log T + 0.00308T + 13.412$  (Newton and Dodge, J. Amer. Chem. Soc. 1934, **56**, 1287; Fracasso, L'Ind. chimica, 1934, **9**, 293).



$\Delta H: -70.8$  (exothermic).

$\Delta F: -55,190 + 24.72T \ln T + 0.0145T^2 - 0.00000037T^3 - 60.74T$  (Smith, l.c.).

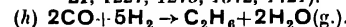


$\Delta H: +51.6$  (endothermic).

$\Delta F: -46,850 + 13.265T \ln T - 0.00633T^2 - 0.00000037T^3 - 31.60T$  (Smith, l.c.).

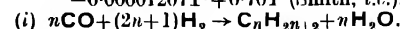
$K_p: ^\circ K$	673	703	723	744	763
$1/-\log K_p$	3.74	3.02	2.56	2.12	1.72

(Ghosh, Chakravarty and Bakshi, Z. anorg. Chem. 1934, **217**, 277; see also Kubelka and Wenzel, Metallbörse, 1931, **21**, 1227, 1275, 1372, 1421).



$\Delta H: -88.1$  (exothermic).

$\Delta F: -81,222 + 14.46T \ln T + 0.01855T^2 - 0.00001207T^3 + 0.70T$  (Smith, l.c.).



The equilibrium relationships given have been determined experimentally and these are more accurate than those calculated from the free energy relationship quoted.

Since nearly all these reactions are exothermic the product depends not so much on the temperature as on the pressure and particularly on the catalyst. In general, hydrocarbons are formed over VIII group metal catalysts. The products range from methane to liquid hydrocarbons as in the Fischer process (Fischer, Brennstoff-Chem. 1935, **16**, 1; Underwood, Ind. Eng. Chem. 1940, **32**, 449), or to solid waxes of high molecular weight (Pichler, Brennstoff-Chem. 1938, **19**, 226). In most instances the reactions are conducted at atmospheric pressure. For a discussion of the mechanism, see Herington and Woodward (Trans. Faraday Soc. 1939, **35**, 958); Craxford (*ibid.* 1939, **35**, 946).

On the other hand, methanol is usually formed over catalysts such as Zn, Cr, almost invariably at high pressures (Smith and Hirst, Ind. Eng. Chem. 1930, **22**, 1037; Z. angew. Chem. 1927, **40**, 166; Pier, Oel u. Kohle, 1933, **1**, 47). By modification of the catalyst, for instance by the

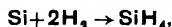
addition of I, VII or VIII group metals, higher primary alcohols are also produced (Graves, *Ind. Eng. Chem.* 1931, **23**, 1381). For the mechanism of these reactions, see Frolich and Cryder (*ibid.* 1930, **22**, 1051), Morgan, Taylor and Hedley (*J.S.C.I.* 1928, **47**, 1177).

**Hydrocarbons.**—Reactions of this type including both the forward and the reverse reactions are very numerous and very important. The following simple types serve merely as examples.

- (a)  $C_2H_4 + H_2 \rightarrow C_2H_6$ .  
 $\Delta H$ :  $-21.4$  (exothermic).  
 $K_p$ :  $1/\log K = -27,798/4.573T + 2.01 \log T - 0.471$  (Frey and Huppke, *Ind. Eng. Chem.* 1933, **25**, 54).
- (b)  $C_3H_6 + H_2 \rightarrow C_3H_8$ .  
 $\Delta H$ :  $-21.7$  (exothermic).  
 $K_p$ :  $1/\log K_p = -25,920/4.573T + 2.01 \log T + 0.047$  (Frey and Huppke, *l.c.*).
- (c)  $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$ .  
 $\Delta H$ :  $-21.6$  (exothermic).  
 $K_p$ :  $\log K_p = 43,850/4.573T - 9.9194 \log T + 2.285 \times 10^{-2}T + 8.565$  (Sharkowa and Frost, *Chem. Zentr.* 1933, **1**, 726).

Metals of the VIII group are frequently, though by no means exclusively, used as catalysts. See Egloff, "Reactions of Pure Hydrocarbons," Rheinhold Pub. Corp., 1937, and Hurd, "The Pyrolysis of Carbon Compounds," *Chem. Cat. Co.*, 1929 (see also this Vol. HYDROGENATION OF COAL).

**Silicon, Boron.**—Direct combination,



occurs at very high temperatures, though the usual method of formation of silanes is by the acid decomposition of magnesium silicide. The silanes comprise a series  $SiH_4$  to  $Si_6H_{14}$ .

Boron and hydrogen do not react, even at high temperatures. The boron hydrides are formed by the action of acid on magnesium boride (*v. Boron*, Vol. II, 40*d*).

**Alkali Metals, etc.**—The alkali metals, the alkaline earth metals (excluding Be and Mg), and many of the rare earth metals react directly with hydrogen, particularly with atomic hydro-

gen, to give solid salt-like hydrides, in which the hydrogen is the anion.

**Metal-Hydrogen Alloys.**—The direct reaction of the above type gradually merges into another type in which the hydrogen is held in an atomic state, as an alloy rather than as a compound. "Copper hydride," for instance, is intermediate between the two types, and there has been much discussion as to whether or not it is a true hydride. Most metals take up some hydrogen, but particularly the rare earths (some of which may be regarded as forming salts), Th, U, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, Pt, Cu, and especially Pd. The alloys are metallic in nature; the solubility of  $H_2$  is increased by pressure, but the effect of temperature depends on the metal. For further details, see papers by Sieverts, *e.g.* *Stahl u. Eisen*, 1914, **34**, 252; *Z. physikal. Chem.* 1907, **60**, 139, 151, 169, 184; *Z. angew. Chem.* 1929, **21**, 37; *Z. physikal. Chem.* 1935, **174**, 359; 1937, **180**, 249; B, **38**, 46.

The hydrides of the elements are classified by Paneth (Ber 1920, **53** [B], 1710) into (a) those in groups 1-4 positions before an inert gas in the periodic system and also boron, which form gaseous hydrides. Here the H is normally linked covalently but, in some instances, *e.g.* HCl in solution, it is ionised as a cation, and in the boron hydrides some of the hydrogen atoms are linked by a singlet bond. (b) Compounds which are like alloys, *e.g.* hydrogen-palladium. (c) Field valency compounds, comprising the compounds with Fe and Ni which are usually classed under (b). (d) Salt hydrides, *e.g.* KH where the H is negatively ionised.

**Metallic Oxides.**—Metallic oxides tend to be reduced by  $H_2$  to the metal. The process occurs readily with oxides of metals low in the electrometric series, where the heat of reduction is considerable and where the necessary temperature is low. On ascending the series, however, the reaction becomes more and more strongly endothermic and the requisite temperature increasingly higher.

In the following list, T (the minimum temperature for reduction) refers to reduction to the metal. Reduction of highly oxidised to less

Metal.	T.	$\Delta H$ .
Sr . . . . .	Electric spark.	+83.2 (SrO) (endothermic)
Th . . . . .	1,100°C. 15 atm.	+107.7 (ThO <sub>2</sub> ) "
Al . . . . .	2,800°	+73.9 (Al <sub>2</sub> O <sub>3</sub> ) "
Mn . . . . .	1,300°	+33.0 (MnO) "
Zn . . . . .	454°	+26.5 (ZnO) "
Cr . . . . .	1,000°	+31.2 (Cr <sub>2</sub> O <sub>3</sub> ) "
W . . . . .	1,100°	+5.9 (WO <sub>3</sub> ) "
Fe . . . . .	305°	+6.2 (FeO) "
Cd . . . . .	300°	+7.5 (CdO) "
Co . . . . .	228°	-0.2 (CoO) (exothermic)
Ni . . . . .	270°	(Ni <sub>2</sub> O) —
Pb . . . . .	235°	-5.3 (PbO) (exothermic)
Bi . . . . .	300°-310°	(BiO) "
Cu . . . . .	155°	-22.9 (CuO) "
Ag . . . . .	100°	-50.8 (Ag <sub>2</sub> O) "
Hg . . . . .	80°	-36.3 (Hg <sub>2</sub> O) "
Pd . . . . .	Without heating.	-36.3 (PdO) "

oxidised oxides occurs at lower temperatures. These data are collected from Gmelin, "Handbuch der anorganischen Chemie," Aufl. 8, System No. 2. The heats of reduction ( $\Delta H$ ) are calculated from International Critical Tables V, and refer to reduction at 18°, 1 atm., per mol. of  $H_2O$  formed.

For further data, see references given above for "Reduction of Water."

#### ACTIVE HYDROGEN.

Many methods have been given in the literature for preparing active modifications of hydrogen, since the original experiments of Wendt and Landauer (J. Amer. Chem. Soc. 1920, **42**, 930). In these experiments bombardment with X-rays, high potential electrical discharge, the corona discharge and the ordinary ozoniser were used, all with positive results.

Other authors have found the following methods effective: desorption from platinum or palladium, or diffusion through a closed palladium tube heated at temperatures up to 800°C; the action of water and heat on metallic hydrides, of acids on metallic magnesium under certain conditions; continuous combustion of oxygen and hydrogen on platinum; electrolysis; electronic bombardment in a thermionic tube, activation by excited mercury atoms (Venkataramaiah and co-workers, Chem. News, 1922, **124**, 323; J. Amer. Chem. Soc. 1923, **45**, 261; Nature, 1923, **112**, 57; Anderson, J.C.S. 1922, **121**, 1153; Grubb, Nature, 1923, **111**, 671; Stead and Trevelyan, Brit. Assoc. Rep. 1923, 425; Taylor and Marshall, J. Physical Chem. 1925, **29**, 1140; Bonhoeffer and co-workers, Z. physikal. Chem. 1924, **113**, 199; 1924, **113**, 422; Z. Elektrochem. 1925, **31**, 521).

Of the methods described, some are not above suspicion. According to Seanavy-Grigoriewa (Z. anorg. Chem. 1926, **159**, 55) positive results with glowing platinum capillaries are probably due to adsorption of  $H_2S$  from the air (cf. also Paneth and co-workers, Z. Elektrochem. 1927, **33**, 102; Copaux, Chim. et. Ind. 1930, **23**, 267).

In general, the active hydrogen produced by these various methods reduces S, Se, Te, P and Sb to their hydrides. Most of these reactions have been studied in some detail by Bagdasaryam (J. Phys. Chem. U.S.S.R. 1937, **10**, 389, 401). Many metallic oxides, e.g. those of W and Cu, are reduced to the metal (Bagdasaryam, *ibid.* 1935, **16**, 1033). Active hydrogen also reduces ethylene, carbon monoxide and oxygen (forming some formaldehyde with carbon monoxide), and reacts with nitrogen to form ammonia. It does not follow, however, that these reactions are general for active hydrogen produced by each of the various methods given.

The active hydrogen produced by X-ray or electronic bombardment, or by electric discharge, possesses in all cases the properties recorded by Wendt and Landauer (*l.c.*), i.e. its activity is removed by liquid air, and a definite volume contraction is noticeable on its formation (Stead and Trevelyan, *l.c.*; Bonhoeffer and co-workers, *l.c.*). According to Hiedemann, however (Z. physikal. Chem. 1931, **153**, 210), the same properties are characteristic of a mixture of silicon hydrides, and all such "active" or

triatomic" hydrogen may be either  $H_2S$  or silicon hydrides—or a mixture of both.

For more comprehensive descriptions of the reactions of active hydrogen, see Hardeck and Roeder (Z. Elektrochem. 1936, **42**, 536—reactions in aqueous solution), Bagdasaryam (Uspekhi Khim. 1936, **5**, 39) and particularly Geib (Ergebn. exakt. Naturwiss. 1936, **15**, 39).

Wendt and Landauer (*l.c.*) consider the properties to be those of triatomic hydrogen, but, although the existence of the ion  $H_3^+$  is probably beyond dispute, there is as yet no definite evidence of the existence of neutral  $H_3$  (Paneth and co-workers, *l.c.*).

It appears probable that hydrogen activated by the electric discharge is monatomic, not triatomic. If a long, wide discharge tube is used at low pressures, as shown by Wood (Phil. Mag. 1921, [vin], **42**, 729), the secondary spectrum, characteristic of molecular hydrogen, is confined to the ends of the tube, and the centre of the tube gives only the Balmer series, characteristic of atomic hydrogen. If the hydrogen is dry, the Balmer series is suppressed. Experiments by Boehm and Bonhoeffer (*l.c.*) have demonstrated fairly conclusively that this active form is atomic hydrogen. The bulb of a thermometer moistened with a salt solution, and held in the gas stream, shows a rise in temperature, due to the reformation of molecular hydrogen. The formation of  $H_2O_2$  with oxygen, and  $HCHO$  with carbon monoxide, suggest the presence of free atoms, while the immediate destruction of the active form by  $HCl$ ,  $HBr$ , etc., is thought to be due to the reaction  $H + HCl = H_2 + Cl$ . It has been shown, however, that hydrogen exposed to electronic bombardment will reduce copper oxide in the cold as soon as the potential applied to the electrons exceeds 1.4 volts. This is exactly the first resonance potential of the hydrogen molecule, and it is therefore possible that "excited" molecules may form a part of "active" hydrogen (Glockner, Baxter and Dalton, J. Amer. Chem. Soc. 1927, **49**, 58).

One form of "active" hydrogen is beyond doubt atomic. This form, the discovery of which is due to Langmuir, is produced by an incandescent tungsten filament heated above 1,300°K. in an atmosphere of hydrogen, or by an electric discharge between tungsten electrodes (Langmuir, *ibid.* 1912, **34**, 1310; 1914, **36**, 1708; 1915, **37**, 417; 1916, **38**, 1145; Ind. Eng. Chem. 1927, **19**, 667).

The abnormal rate at which heat is conducted from such a filament at temperatures above 1,700°K. (the heat carried away is proportional to  $T^{1.9}$  for most gases and for hydrogen up to 1,700°K., but increases more rapidly above this temperature until at 2,600°K. and above, it is proportional to  $T^5$ ) led to the conclusion that strong dissociation of  $H_2$  must take place under such conditions.

Data at higher pressures have demonstrated conclusively that atomic hydrogen H, and not  $H_3$ , is responsible for the abnormal conductivity effect.

Atomic hydrogen produced by the Langmuir method reacts rapidly with oxygen at room temperatures and slowly even at liquid-air temperatures. It reduces oxides of tungsten, copper,

iron ( $\text{Fe}_2\text{O}_3$ ) and zinc. No atomic hydrogen, however, passes through a trap cooled in liquid air. Ethylene is decomposed to form acetylene, benzene and other hydrocarbons being formed in smaller quantity (Von Wartenberg and Schultze, *Z. physikal. Chem.* 1929, B, 2, 1; Bonhoeffer and Hardeck, *ibid.* 1928, 139, 64). The life of atomic hydrogen is short, the half-period being about 1 second (Bay and Steiner, *ibid.* 1929, B, 2, 146).

#### THE STRUCTURE OF HYDROGEN ATOMS AND MOLECULES.

The hydrogen (protium) atom consists of a single proton, around which a single electron revolves in an elliptical orbit. Variation can occur in the size of the orbit, but only discontinuously, i.e. there is a finite number of possible orbits. The condition prevailing when the electron is revolving in a given orbit is a "stationary state"; no energy changes occur and the coulomb force between the electrical charges is balanced by the centrifugal force due to the inertia of the electron.

The stationary states may be numbered 1, 2, 3 . . .  $n$  outwards from the nucleus, and are characterised by the fact that in them the electron bears 1, 2, 3 . . .  $n$  quanta of energy, respectively. Thus the energy of the electron at the  $n$ th orbit,  $E = n h \nu$ .

$n$  is an integer denoting the particular orbit.

$h$  = Planck's constant =  $6.554 \times 10^{-27}$  erg-seconds.

$\nu$  = the frequency of rotation.

On transferring from one orbit to another, say from the first to the second, an energy change occurs.

Some of the characteristics of the stationary states for hydrogen are:

Quantum number.	Radius.	Frequency of revolution	Work of removal.	Velocity in orbit
1	1	1	1	1
2	4	1/8	1/4	1/2
3	9	1/27	1/9	1/3
4	16	1/64	1/16	1/4
$n$	$n^2$	$n^{-3}$	$n^{-2}$	

The work of removal of the electron from the  $n$ th orbit to infinity is thus proportional to  $n^{-2}$ , i.e.

$$E_n = \frac{R h}{n^2},$$

where  $R$  is a constant.

The energy radiated when the electron jumps from the  $n$ th orbit is

$$E_n - E_{n_1} = R h \left( \frac{1}{n^2} - \frac{1}{n_1^2} \right) = h \nu$$

or  $\nu = R \left( \frac{1}{n^2} - \frac{1}{n_1^2} \right)$

When  $n=1$  and  $n_1=2, 3, 4 \dots$  the resulting series of spectrum lines constitutes the Lyman Series; when  $n=2$  and  $n_1=3, 4, 5 \dots$  the Balmer Series occurs; when  $n=3$  and  $n_1=4, 5, \dots$  the Paschen Series occurs; and when  $n=4$  and  $n_1=5, 6, 7 \dots$  the Brackett Series results.

The constant

$$R = \frac{2\pi^2 N^2 e^4 m}{ch^3} = 1.09675 \times 10^5$$

where  $m$  = the mass of the electron  
 $e$  = the charge on the electron  
 $N$  = the charge on the nucleus  
 $c$  = the velocity of light.

Owing to the fact that the orbits are elliptical, the velocity of the electron varies with its position, and hence the energy varies. This results in each of the spectrum lines becoming spread and really consisting of a number of "fine spectrum" lines.

The number of atomic and molecular structures, accorded the title of "hydrogen" has greatly increased during recent years. The nomenclature and symbols of these structures are as follows:

Let "hydrogen" be represented by

$$w - {}^y_x \text{H}_z$$

In the position of " $w$ " the prefix " $o$ " (ortho), " $p$ " (para), " $e$ " (equilibrium between  $o$  and  $p$ ) or " $n$ " (normal in relation to " $o$ " and " $p$ "), i.e. in equilibrium at ordinary temperatures) gives the condition of the molecule in relation to nuclear spin. When omitted,  $n$  may be assumed. The subscript in the position of " $x$ " gives the atomic number. This is 1 in the case of hydrogen and is frequently omitted.

The superscript in the position " $y$ " gives the atomic weight relative to hydrogen (protium), i.e.  ${}^1\text{H}$  is the hydrogen (protium) atom;  ${}^2\text{H}$  or  $\text{D}$  is the deuterium atom;  ${}^3\text{H}$  or  $\text{T}$  is the isotope atom of mass 3, tritium;  ${}^4\text{H}$  is the isotope atom of mass 4. When omitted it may be assumed that a mixture is meant with the "natural" amount of deuterium, i.e. 5,000  ${}^1\text{H}_2$  to  $\text{D}_2$  and negligible amounts of higher isotopes.

The subscript in position  $z$  represents the number of atoms in the molecule, i.e.  $\text{H}$  (atom),  $\text{H}_2$  (ordinary diatomic molecule),  $\text{H}_3$  (triatomic molecule, *hyzone*).

In addition the usual + or - indicates positive or negative ionisation.

**Ortho- and Para-Hydrogen.**—In the hydrogen atom, both the electron and the proton which comprises the nucleus have two possible directions of spin. The electron spins of any pair of  $\text{H}$  atoms may therefore be parallel or anti-parallel, and similarly with the protons. Only those atoms with anti-parallel electron spins, however, are able to enter into combination, so there occurs in the hydrogen molecule two possible spin isomers—those with parallel nuclear spins (ortho-hydrogen), and those with anti-parallel nuclear spins (para-hydrogen). The

existence of these two modifications was experimentally demonstrated by Bonhoeffer and Harteck (Naturwiss, 1929, 17, 182).

A further difference between the isomers is that in the para-molecule only the even rotational levels are occupied, whereas in the ortho-molecule it is only the odd levels. Consequently at extremely low temperatures when all the molecules tend to pass into the lowest rotational level ( $J=0$ ), equilibrium lies entirely on the side of para-. At infinitely high temperature the equilibrium lies at 3 ortho:1 para-. Equilibrium is, however, only reached under favourable conditions and the mixture occurring at

normal temperatures (which approximates very closely to 3 ortho:1 para-) may be cooled to low temperature without change in composition. Distinction may therefore be drawn between this normal mixture ( $n\text{-H}_2$ ) and the equilibrium mixture ( $e\text{-H}_2$ ), as well as between the pure  $o\text{-H}_2$  and  $p\text{-H}_2$ . The following table taken from Farkas ("Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, 1935) shows the rotational levels occupied at different temperatures. The sum of the even  $J$  numbers and the sum of the odd  $J$  numbers for  $e\text{-H}_2$  indicate also the equilibrium amounts of para- and ortho- respectively.

Temp. °K.	Hydrogen.	$J=0$ .	$J=1$ .	$J=2$	$J=3$	$J=4$ .	$J=5$ .
50	$e\text{-H}_2$	76.88	23.11	0.01	—	—	—
	$p\text{-H}_2$	99.98	—	0.02	—	—	—
	$o\text{-H}_2$	—	100.0	—	—	—	—
	$n\text{-H}_2$	24.995	75.00	0.005	—	—	—
100	$e\text{-H}_2$	37.36	61.46	1.15	0.02	—	—
	$p\text{-H}_2$	97.02	—	2.98	—	—	—
	$o\text{-H}_2$	—	99.95	—	0.05	—	—
	$n\text{-H}_2$	24.25	74.97	0.74	0.03	—	—
200	$e\text{-H}_2$	18.65	71.67	7.27	2.38	0.03	0.002
	$p\text{-H}_2$	71.82	—	28.05	—	0.13	—
	$o\text{-H}_2$	—	96.78	—	3.21	—	0.003
	$n\text{-H}_2$	17.95	72.59	7.01	2.41	0.03	0.002
300	$e\text{-H}_2$	12.89	65.78	11.78	9.07	0.40	0.08
	$p\text{-H}_2$	51.40	—	47.00	—	1.59	—
	$o\text{-H}_2$	—	87.80	—	12.10	—	0.10
	$n\text{-H}_2$	12.85	65.84	11.75	9.08	0.40	0.08

Pure para-hydrogen is prepared by converting  $n\text{-H}_2$  to  $e\text{-H}_2$  (i.e.  $p\text{-H}_2$ ) at liquid-air temperatures, using active charcoal or Nikieselgular catalyst (Bonhoeffer and Harteck, Naturwiss, 1929, 17, 182; Z. physikal. Chem. 1929, B, 4, 113; B, 5, 292; Z. Elektrochem. 1929, 35, 621; Taylor and Sherman, Trans. Faraday Soc. 1932, 28, 247). It is impossible to convert  $n\text{-H}_2$  into  $o\text{-H}_2$ , since at no temperature does the equilibrium lie entirely on the  $o\text{-H}_2$  side, and failing a physical method of separation, pure  $o\text{-H}_2$  cannot be prepared. For the heat of transformation, see Elbe and Simon (Z. physikal. Chem. 1930, B, 6, 79).

The composition of  $o\text{-}p\text{-H}_2$  mixtures is conveniently estimated by thermal conductivities (Bonhoeffer and Harteck, *ibid.* 1929, B, 4, 113).

The following properties of  $p\text{-H}_2$  may be compared with those of  $n\text{-H}_2$ :

	$n\text{-H}_2$ .	$p\text{-H}_2$ .
Boiling-point °K. . . .	20.37*	20.26†
Triple point °K. . . .	13.94*	13.83†
Vapour pressure mm.—		
20–18°K. . . . .	708.2‡	732.9‡
17–18°K. . . . .	250.5‡	261.7‡
15–18°K. . . . .	108.7‡	103.5‡

\* See above under "Physical Properties of Hydrogen."

† Bonhoeffer and Harteck, Z. physikal. Chem. 1929, B, 4, 113; see Farkas (*op. cit.*).

‡ Keesom, Bijl and Horst, Proc. K. Acad. Wetensch. Amsterdam, 1931, 34, 1223; see Farkas (*op. cit.*).

#### Heavy Hydrogen—Deuterium (*q.v.*).

**Other Isotopes of Hydrogen.**—In the reaction,  $^2\text{D} + ^2\text{D} \rightarrow ^3\text{H} + ^1\text{H}$ , a hydrogen isotope of mass 3 is formed (Dec, Nature, 1934, 133, 564).

The possibility of the higher isotope of mass 4 has been discussed by Flugge (Z. Physik, 1937, 105, 522).

**Triatomic Hydrogen (Hyzone).**—One of the theories explaining the activity of "active" hydrogen is that it is triatomic. Actually the existence of a neutral triatomic molecule  $\text{H}_3$  is under considerable doubt (see e.g. Smallwood and Urey, J. Amer. Chem. Soc. 1928, 50, 620). The ion  $\text{H}_3^+$  however is known to exist and was first observed by J. J. Thomson in canal rays. He claimed later (Phil. Mag. 1934, [vii], 17, 1025) that two kinds exist, the one formed by passing the discharge through ordinary hydrogen is very unstable, the other, formed by bombarding solid KOH with electrons and passing a discharge through the evolved gases, is fairly permanent. When KOD is used,  $\text{H}_4$  is also present (as well as  $\text{H}_3^+$  and  $\text{H}_3$ ).

**HYDROGEN BIBLIOGRAPHY.**—Further details on the properties and reactions of hydrogen can be found in the following sources. Much of the data given there, however, has been amplified or corrected by more recent work:

Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, 1922.



Newton Friend, "Textbook of Inorganic Chemistry," Vol. II, 1924.

Abegg, "Handbuch der anorganischen Chemie," 1908, Band II, Abt. 1.

Gmelin, "Handbuch der anorganischen Chemie," Aufl. 8, 1927, System No. 2.

Pascal, "Traité de Chimie minérale," Vol. I, Masson, Paris, 1931.

International Critical Tables 1926-1933.

Tables Annuelles Internationales de Constantes et Données Numériques.

### TECHNICAL PRODUCTION.

*General Literature.*—From 1918-21 a number of books were published dealing with the commercial production and usage of hydrogen, and they form excellent summaries of the state of development of the various processes up to the time they were written. These books are therefore valuable for early history of the subject, including patent references, and the following may be cited:

Martin, "Industrial Gases" (Crosby Lockwood & Son), 1918.

Teed, "The Chemistry and Manufacture of Hydrogen" (Edward Arnold), 1919.

Greenwood, "Industrial Gases" (Baillière, Tindall & Cox), 1920.

H. S. Taylor, "Industrial Hydrogen" (Chemical Catalogue Co., U.S.A.), 1921.

For reference on the subject from the standpoint of ammonia synthesis, see AMMONIA, Vol. I, 331d, and from the standpoint of hydrogenation, see Groggins, "Unit Processes in Organic Chemistry" (McGraw-Hill Book Co.), 1935, Chapter VIII, Hydrogenation (Fenske). Two general articles covering the whole field of commercial hydrogen production are Brownlie, Ind. Eng. Chem. 1938, 30, 1139, and Heinrich, Chem.-Ztg. 1933, 57, 933-934, 950-952. Apart from the above, the original references and the patents quoted must be consulted to obtain more information on the processes dealt with below.

The various processes used commercially for the production of hydrogen may be classed as follows:

- (1) Electrolytic Decomposition of Water.
- (2) Direct Reduction of Steam by Carbon.
- (3) Indirect Reduction of Steam by Carbon, Using an Intermediary.
- (4) Reduction of Steam by Hydrocarbons.
- (5) Cracking of Hydrocarbons.
- (6) Hydrogen Recovery from Commercial gases (e.g. Coke-Oven Gas) by Partial Liquefaction.
- (7) Production of By-product Hydrogen.

#### (1) ELECTROLYTIC DECOMPOSITION OF WATER.

Before oxygen and hydrogen can be evolved from the electrodes of an electrolytic cell, the

applied E.M.F. must overcome three opposing forces: (a) the reversible decomposition voltage of water, which is 1.23 volts, (b) the actual resistance of the electrolyte, (c) the  $O_2$  and  $H_2$  over-voltages at the anode and cathode respectively, both of which rise with increasing current density. The aims of commercial cell design are to reduce (b) and (c) to as low a figure as is practicable, to keep separate the hydrogen and oxygen, to avoid corrosion of the electrodes, and to minimise current leakage, electrolytic leakage, and repair requirements. In commercial practice (a), (b) and (c) total 2 to 4 volts. To keep (b) at a minimum, the electrolyte most commonly used is KOH, sometimes NaOH, at as high a concentration and temperature as possible, consistent with avoiding corrosion. Early type cells (e.g. Schoop cell) employed  $H_2SO_4$ , but these are now almost obsolete. Electrolyte concentration is usually 20% NaOH or 20-25% KOH, and the operating temperature up to 70°C. Since the E.M.F. dissipated in overcoming (b) and (c) above appears as heat, the temperature is maintained without additional heating, and in many cases provision for cooling must be made. A further method of reducing (b) is to bring anode and cathode as close as possible, but the limit here is set by the necessity of keeping oxygen and hydrogen separate.

Electrodes are usually of mild steel, and to reduce (c) above and at the same time to avoid

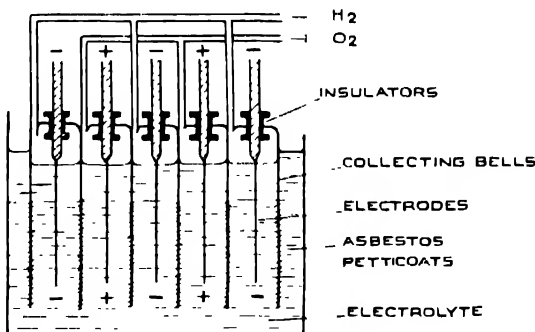


FIG. 1.

corrosion, the anodes and, in many cases the cathodes also, are nickel plated. In the *Levin* or *Electrolabs* cell cobalt plating is used. Other methods of reducing (c) are special treatment of electrode surfaces, and decrease of electrode current density by the provision of subsidiary electrodes held away from the main electrode by small metallic studs (e.g. the *Bamag Zdansky* battery).

Two main types of cell have been developed to ensure the separation of anode and cathode gases:

- (a) The open or bell type, in which gases are collected in bells placed above the electrodes. Asbestos "petticoats" are fixed round the bottom of the bells to improve separation (Fig. 1). Examples: *Fausser*, *Knowles* and *Holmboe*.
- (b) The enclosed or filter press type in which

the walls of the vessel containing the electrolyte themselves serve as electrodes. In this case a battery of cells is formed by vertical electrodes kept apart from one another by insulating material along their edges, with diaphragms alternating with the electrodes for keeping separate the oxygen and hydrogen. The cells are completely filled with electrolyte, and on passing current from one end of the battery to the other, each electrode acts as cathode on one side and anode on the other (Fig. 2). Some of the advantages of this type are that a single battery may contain up to 160 cells in series, permitting the use of high voltages without the necessity of copper conductors to connect a like number of bell-type cells in series. As the electrolyte is not exposed to the atmosphere,  $\text{CO}_2$  absorption is avoided, and the floor space required is usually smaller than with bell-type cells. The diaphragms may be of perforated nickel sheet ("Pechkranz"), asbestos, or asbestos with steel wire inlay ("Bamag"). Other

separated from the cathode by vertical diaphragms.

The electro-chemical efficiency of all commercial electrolyzers approaches 100%; the slight inefficiency is not due to unwanted chemical reactions, but to the small leakage of current through the insulation. The water supplied to the cells must be very pure. Chloride impurities are particularly undesirable since they may lead to corrosion of the anodes. Any suspended iron in the feed water will deposit on the cathodes and build across to the diaphragm causing this to act as a cathode, resulting in hydrogen impurity in the oxygen.

The purity of the electrolytic gases is normally  $\text{H}_2$  99.5-99.8%,  $\text{O}_2$  98.5-99.0%. Decrease of purity may be due to the causes given above, or to the rupture of the diaphragms. Where very high-purity gases are required (e.g.  $\text{H}_2$  for ammonia synthesis) they may be obtained by passing the  $\text{H}_2$  over a catalyst such as platinised asbestos or copper, when the oxygen impurity burns to water and is condensed.

The labour requirement for the electrolytic process is small, and correctly designed cells or batteries may be operated 5 years or longer without need of repair. With open type cells, carbonation of the electrolyte may necessitate installation of a causticising plant; regulation of the feed water to these cells may also present difficulty, because with variation of the gas pressure inside the bells, overflow of electrolyte may occur. With certain types of cells it is necessary at intervals to remove deposits of spongy iron from the cathodes, clean the diaphragms and replat the anodes. The principal operating cost is power, which may vary from 5.0 to 6.0 kw.h. per cu. m. of  $\text{H}_2$  plus  $\frac{1}{2}$  cu. m. of  $\text{O}_2$ . Owing to the fall in overvoltage on lowering the current density, the power consumption per cubic metre of hydrogen of an electrolytic plant will fall with reduction of output. Published figures may therefore be misleading, and for a given output the relative merits of different designs can only be determined by comparison of power requirements at similar capital costs. Alternatively, comparison of capital costs should be made with plant of similar efficiencies. It follows also that the economic size of an electrolytic plant will depend on the cost of power, because for a given hydrogen output, capital expended on increasing the number of cells or batteries will decrease the power requirement.

Pressure electrolyzers have been proposed and developed on a semi-technical scale by Noeggerath, Niederreither and others, to operate up to 150 atm. pressure. It is claimed that the increase in pressure reduces the oxygen and hydrogen overvoltages, with consequent reduction in power requirements. Thus it may be said that the electrical energy fed to the cell appears partly as compression energy in the gases evolved, instead of as heat. Clearly one of the major problems arising in the design of a pressure electrolyser will be to avoid any marked difference of pressure at the cathode and anode. The power required to compress oxygen or hydrogen is small compared with that used in the process of electrolysis. Thus in spite of

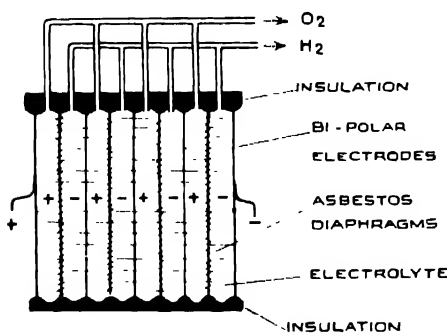


FIG. 2.

examples of the filter press type are Schmidt-Oerlikon, Siemens, Roth (I.G.) and the National Electrolyser. Metallic diaphragms are permissible unless the voltage applied across the cell is so high (i.e. about 4 volts) that the potential difference between one electrode and the diaphragm exceeds the decomposition voltage of the electrolyte. Then the diaphragm itself will act as an electrode, and impure gases will be obtained. The principal difficulty in the construction of the filter press type is to obtain a material suitable for insulation between the electrodes which at the same time is not attacked by the electrolyte, and does not allow electrolyte leakage.

The Levin or Electrolabs cell is of the enclosed type, but in this case the electrodes are separate from the walls of the containing vessel, being electrically insulated at the point where the electrode connections pass through the electrolyte container. The cathode is a central vertical plate, and there are two anodes, one on either side. The anodes are

advocacy of the use of pressure cells as a method of storing off-peak electrical power, no large installations have been reported.

The modern tendency of battery design is to obtain a greater output for a given capital cost by increasing the operating current density. This necessitates increased provision for cooling. In the *Bamag Zdansky* battery the electrolyte is circulated by the lifting effect of the bubbles of gas evolved, and the liquor circuit includes coolers and filters. It is claimed that this system reduces the oxygen and hydrogen overvoltages and prevents iron deposits on the cathodes.

*Literature* — Allmand and Ellingham, "Applied Electro-chemistry" (Edward Arnold), 1924, pp. 458-464, discuss the following types: *Schoop, Knowles, Integral Oxygen, Lervn or Electrolabs, International Oxygen, Schmidt-Oerlikon, Geeraard or Churchill*. Takimenko, Khmistroi, 1934, 6 and 7, describes and gives operating data for the following: *Bamag Zdansky, Fauser, Knowles, Pechkranz, Steward, Kent, Siri*. See also H. S. Taylor, "Industrial Hydrogen"

(Chemical Catalogue Co., U.S.A.), 1921. Zdansky, Chem. Fabrik. 1933, 6, 49, describes the *Bamag Zdansky* battery and gives operating costs. Diamond, Trans. Inst. Min. Met 1934, 442-460, describes electrolytic hydrogen plant at Trail, B.C., and *Knowles, Fauser, Stuart* and *Pechkranz* batteries. Noeggerath, Chem. Met. Eng. 1928, 35, 421, and Heinze, Engineering, 1933, 185, 399. Niederreither, G.P. 600583 and U.S.P. 1983294.

## (2) DIRECT REDUCTION OF STEAM BY CARBON.

The commonest industrial reducing agent for obtaining  $H_2$  from steam is carbon in the form of coke. In the so-called *Water-gas catalytic* process, the reaction takes place in two stages, the first of which involves reaction of a solid, and the second is entirely gaseous.

- (a)  $C + H_2O \rightleftharpoons CO + H_2$ ;  $\Delta H + 31.4 \text{ kg.-cal. per g.-mol. (endothermic)}$ .  
 (b)  $CO + H_2O \rightleftharpoons CO_2 + H_2$ ;  $\Delta H - 10.1 \text{ kg.-cal. per g.-mol. (exothermic)}$ .

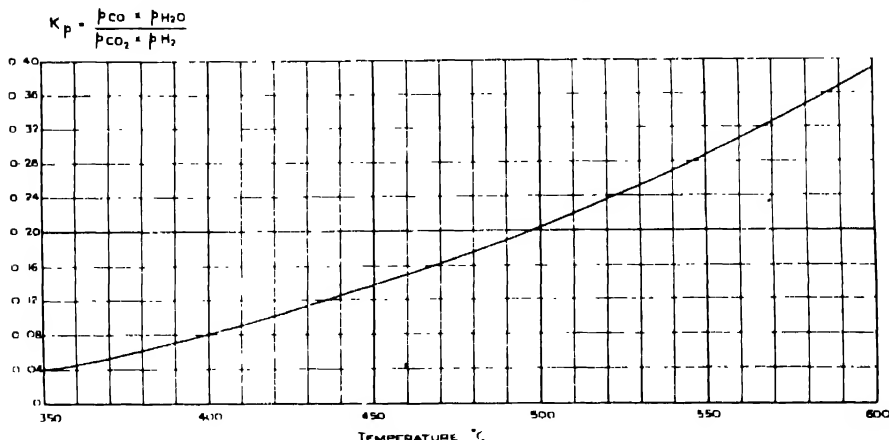


FIG. 3.—EQUILIBRIUM CURVE (NEUMANN AND KÖHLER) OF THE WATER-GAS REACTION.  
 $CO + H_2O \rightleftharpoons CO_2 + H_2$ .

The first reaction is that which takes place in a standard blue water-gas generator (see Gas, WATER). The second is carried out at a temperature of 400-550°C. over a pelleted catalyst of iron oxide containing promoters. The equilibrium for the so-called water-gas reaction (b) is stated on p. 318c. Fig. 3 gives the values of the equilibrium constant over the usual operating range of temperatures. The lower the temperature, the greater the equilibrium hydrogen content. Hence it is usual to carry out the reaction in two stages, firstly at 500-600°C., where the high temperature favours a rapid approach to equilibrium, and then at a lower temperature 400-500°C., where, because of the more favourable equilibrium, the reaction proceeds further. The resulting plant is as given in Fig. 4. The catalyst is brought up to operating temperature by burning air in water-gas at the top of one or both converters. With

adequate heat exchange and insulation the system maintains its own temperature, and in practice some of the heat of reaction and some of the unconverted steam are recovered by heating water with the hot converted gas after it leaves the final interchanger. This hot water is then used to heat and saturate with water vapour the unconverted water-gas before it passes to the heat exchanger (v. Vol. V, 496a). The range of steam : water-gas ratios most commonly employed is 3:1 to 1:1 by volume. The higher the steam ratio, the lower the CO content of the converted gas, which in practice varies from 5 to 1% CO.

The reaction is usually carried out at a pressure of 1-2 atm. absolute, although some plants operate at higher pressures. The equilibrium is no more favourable than at lower pressures, but it is more quickly attained. The catalyst is contained in mild steel vessels and is supported

on trays in a manner similar to that used for the catalyst in the contact method of oxidising  $\text{SO}_2$ . A number of catalysts have been patented which improve the equilibrium by absorbing the  $\text{CO}_2$  produced, but no large scale installations operating on this principle are reported. The original Badische (now the I.G.) units had a capacity of 25,000 cu. ft. per hour although very much larger units are now common.

With most of the catalysts employed industrially, removal of  $\text{H}_2\text{S}$  from the inlet water-gas improves the catalyst activity and lowers the  $\text{CO}$  content of the exit gas. The standard iron-oxide box process is commonly used for  $\text{H}_2\text{S}$  removal, and a recent development has been the construction of tower purifiers which utilise a very active oxide mass and can be rapidly emptied and refilled. Active carbon

removal, solutions of organic bases may be used which are regenerated by heating (the *Girbotol* and the *Alkacid* (I.G.) processes). The requirements for the absorbing solution are that its volatility should be low to avoid losses, that the  $\text{CO}_2$  capacity of the solution should be high, and that the  $\text{CO}_2$  partial pressure above a carbonated solution should be low at room temperatures, but to effect easy regeneration should rise rapidly with increase in temperature. These processes for  $\text{CO}_2$  removal are to be preferred where the final gas mixture is not required at pressure (e.g. the *Fischer-Tropsch* process, see later).

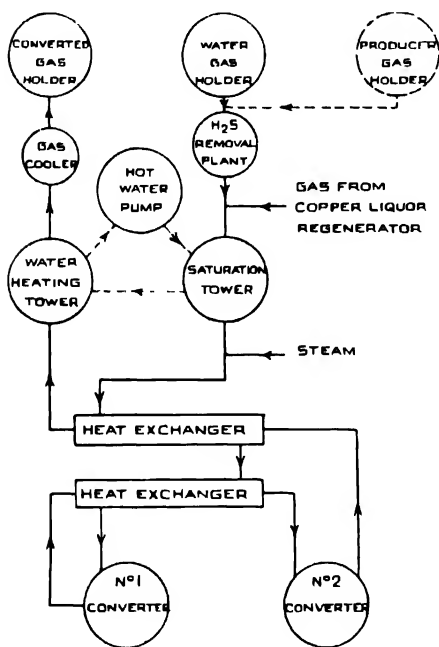


FIG. 4.

can also be employed for oxidising  $\text{H}_2\text{S}$  to  $\text{S}$  and  $\text{H}_2\text{O}$ , and there are a number of wet processes usually involving gas-scrubbing with iron oxide suspensions or alkaline solutions (examples—*Ferror*, *Thylor*, *Koppers*, etc.). The solution is regenerated by aeration, and the  $\text{H}_2\text{S}$  is oxidised, liberating a sulphur scum which may be recovered from the surface of the solution.

To obtain pure hydrogen from the converted gas,  $\text{CO}_2$  is removed usually by water-scrubbing at pressures from 10–50 atm. The scrubbing water is freed from  $\text{CO}_2$  by air-stripping and is used again. With large plant the energy expended on injecting the water into the scrubbing tower is frequently partly recovered by passing the water from the tower through a Pelton wheel or other form of water-motor (Fig. 5). As an alternative to water-scrubbing for  $\text{CO}_2$

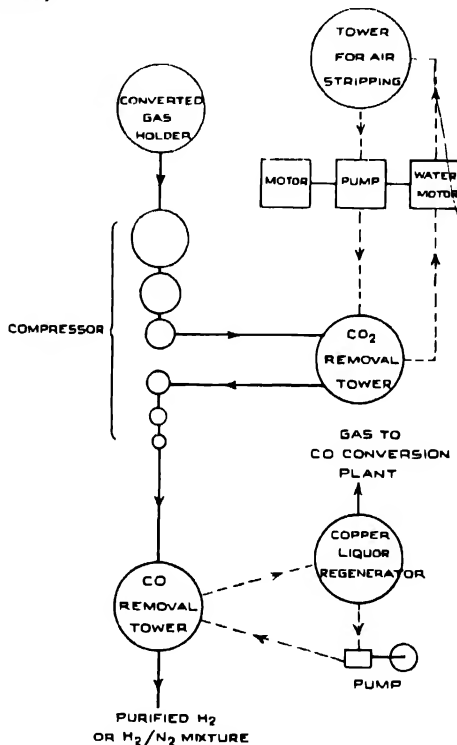


FIG. 5.

The  $\text{CO}$  not converted in the conversion stage, and any  $\text{CO}_2$  still remaining, are removed at still higher pressures by scrubbing with an ammoniacal cuprous salt solution, which is regenerated for further use by heating. The gas given off during regeneration consists largely of  $\text{CO}$ , and is returned to the inlet of the  $\text{CO}$  conversion unit. Thus all the  $\text{CO}$  entering the system is finally oxidised to  $\text{CO}_2$ , and the ratio of water-gas required to pure hydrogen obtained is very little above 1:1. The impurity remaining in the final gas is nitrogen contained in the original water-gas. For ammonia synthesis where a final  $\text{H}_2:\text{N}_2$  ratio of 3:1 is required, producer gas is added before the  $\text{CO}$  conversion plant or semi-water-gas may be employed.

The most recent developments have been not in the  $\text{CO}$  conversion or purification stages of

the process, but in the production of the water-gas. Coal is frequently a cheaper starting material than coke, and may therefore be preferred. Processes utilising coal have the additional advantage that the hydrogen in the coal is also usefully recovered. The disadvantages are the production of tar and the presence of hydrocarbons in the water-gas. For many purposes (e.g. the synthesis of ammonia) even small amounts of hydrocarbons are a serious drawback, because they build up in the synthesis system and must be purged therefrom, resulting in the simultaneous loss of considerable quantities of hydrogen. Thus the aim of the coal-gasification processes is to destroy the tar and hydrocarbons given off as the coal is heated, by cracking or decomposition with steam, before they pass to the exit gas. This is achieved by passage of the hydrocarbons

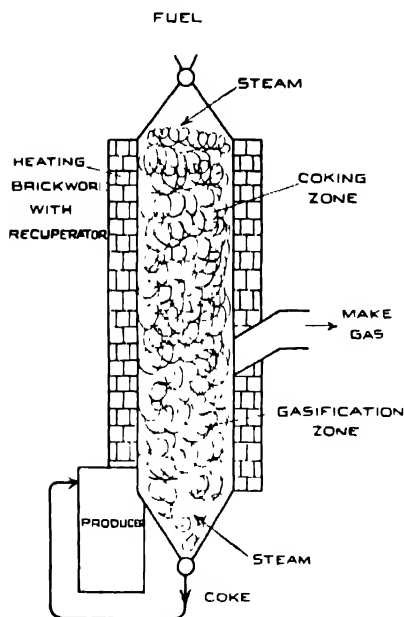


FIG. 6.

through a hot zone, which is frequently the incandescent coke formed after the initial heating of the coal. For processes making gas for the *Fischer-Tropsch* process an additional objective is the production in one stage of a gas containing the required  $H_2:CO$  ratio of 2:1.

In general, coal-gasification processes are most easily applied to brown coals and lignites, because these produce very active cokes after initial heating. The following are typical examples:

The *Winkler* Generator is described under GAS, WATER (Vol. V, 501). The hydrocarbons are cracked in the fuel bed itself or in the large hot gaseous zone above the bed, into which secondary air is introduced. For the final production of  $H_2$ , or  $3H_2+N_2$  for ammonia synthesis, an oxygen-enriched air is used. The oxygen cost is a disadvantage.

The *Bubiag Didier* Retort (Fig. 6).—In this plant the heat necessary for the gasification of coal with steam passes to the fuel bed through the walls of a bench of brickwork retorts very similar to standard gasworks vertical retorts. Steam is added at the top and bottom of each retort, and the gas exit is about one-third of the way from the bottom. Fuel is added at the top, and thus the tar and hydrocarbons given off in the upper or coking zone of the retort must pass through the hot coke in the centre of the retort before they pass to the exit main. They are hereby cracked or decomposed with steam. The unreacted coke from the bottom of the retorts is fed to producers heating the retorts. An exit gas containing <1.0% methane is claimed, and the process is suggested as particularly suitable for *Fischer-Tropsch* gas, owing to the ease of control of the  $CO:H_2$  ratio.

The *Viag* Generator (*Ver gasungs-Industrie A.-G.*) (Fig. 7).—This is in effect a twin water-gas generator fed with coal. On the down run the gases given off in the coking or upper zone of the generator pass through the coke bed and are thereby decomposed. On the up run the hydrocarbons pass forward with the make gas, but decomposition is assured by passage down through the incandescent coke bed of the twin

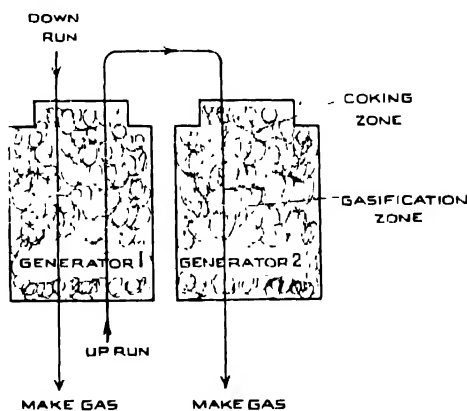


FIG. 7.

generator. Periodically steam is shut off from each generator in turn and a blast of air admitted as in standard water-gas practice. Recuperators are used to improve the heat efficiency of the process.

The *Pintsch-Hillebrand* Generator is also described under GAS, WATER (Vol. V, 502), but the principles of operation are shown in Fig. 8. In this case the hydrocarbons are decomposed firstly in the recuperator (or regenerator) and then in the fuel bed.

The *Lurgi* Process.—This process utilises oxygen for gasification of brown coal at about 10 atm. pressure. A somewhat similar process has been proposed by Fauser. The advantage claimed for pressure operation is that it enables the fuel bed to be operated at a lower temperature. Thus, for example, for *Fischer* synthesis a gas of suitable composition may be obtained

in one stage. As there is no special attempt to crack or decompose hydrocarbons, the methane content of the make gas is higher than with other processes, but it is nevertheless suitable for *Fischer* synthesis. As with the *Winkler* process the cost of oxygen will be a disadvantage.

**Literature.**—For general description and operating costs of stages of process employing coke water-gas, see Laupichler, *Chem. Met. Eng.* 1936, **43**, 122, and *Gas World*, 1936, **105**, 71. Held, *Petroleum*, 1939, **35**, 435, discusses production of ammonia-synthesis gas from coal and describes *Pintsch-Hillebrand*, *Didier*, *Lurgi*, *Wintershall-Schmalfeldt* and *Koppers* processes. Schultes, *Gluckauf*, 1936, **72**, 273, gives cost estimates for production of *Fischer* synthesis-gas by numerous processes, and describes *Winkler*

and *Didier* processes; see also Giordani, *J. Usines Gaz*, 1937, **61**, 170, 196, 229. Müller, *Chemical Engineering Congress, World Power Conference*, 1936, Paper 5E, discusses complete gasification of coal and describes the *Pintsch-Hillebrand* process. For *Didier* process, see Szigethy, *Z. Ungar. Ing. u. Arch. Verein*, 1934, **37** and **38**, and Than, *Brennstoff-Chem.* 1935, **18**, 61. Complete gasification with oxygen, Fauser, *11th International Congress Pure and Applied Chemistry, Madrid*, 1934; Drawe, *Gas-u. Wasserfach*, 1933, **76**, 541, and Blackburn, Williams and Millett, *Inst. Gas Engineers*, 1936, Communication No. 141. Van der Werth, *Chem.-Ztg.* 1935, **59**, 276, reviews German patents covering CO conversion. Tower purification process, Lenz and Borchardt, *Gas-u.*

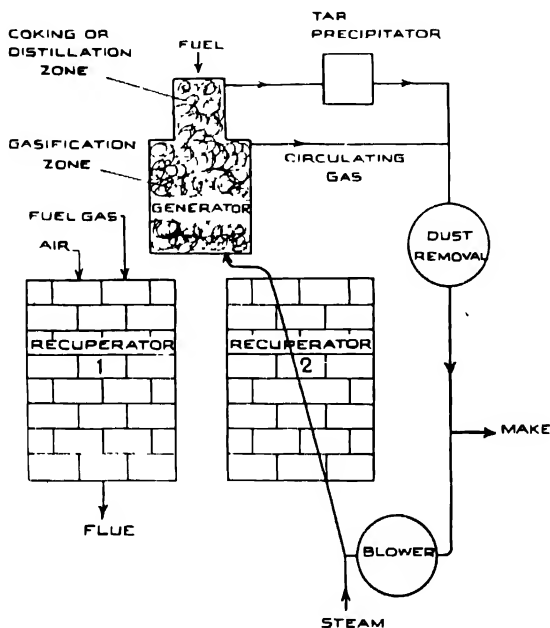


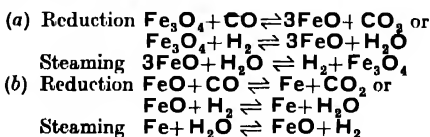
Fig. 8.

*Wasserfach*, 1933, **74**, 445. *Alkacid* process, Bähr, *Proc. Amer. Petroleum Inst. 8th Mid-year Meeting, Sect. III*, 1938, **19**, 37.

### (3) INDIRECT REDUCTION OF STEAM WITH CARBON USING AN INTERMEDIARY.

**The Iron-Steam Process.**—In this process oxides of iron form the intermediary in reducing steam with carbon. The carbon is first converted into water-gas or producer-gas by the standard process, and the gas is used at temperatures varying from 550°C. to 750°C. to reduce oxides of iron, generally in the form of spathic ore, because this is porous and at the same time robust. Silica is undesirable in the ore since it forms a glaze which prevents reaction. The reducing gas is then shut off and steam is passed over the oxide mass, resulting in the oxidation of

the mass and the production of hydrogen. The equations can be written:

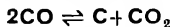


The process is thus a cyclic one, the reduction stage being endothermic and the steaming stage exothermic. When reduction is by CO, the final result is the reaction of steam with CO as in the water-gas catalytic process already described, and thus there is a net heat evolution. Nevertheless the inevitable heat losses from any industrial plant are such that heat must be continually supplied to the system, and this is usually obtained by burning spent water-gas

obtained during the reducing stage, which from equilibrium considerations still contains a considerable percentage of combustibles. The combustion of producer-gas has been suggested as an alternative source of heat, and partly burnt coke-oven gas or even coal dust have been proposed as alternatives to water-gas for the reducing stage.

Taylor (*op. cit.*) has shown that from published data on iron oxide- $\text{H}_2$ - $\text{CO}$  equilibria, reaction (a) above will require less water-gas than (b) to produce the same amount of hydrogen, although it is clear from the equations that for a given amount of iron (b) would be expected to give the greater hydrogen output. Further, assuming reaction (a) and quite apart from the gas that it is necessary to burn to maintain temperatures, the equilibria involved necessitate that at  $750^\circ\text{C}$ . the minimum possible ratio of water-gas consumed to hydrogen produced is 1.6:1. In actual practice this ratio will be 2 to 3:1. A method of overcoming equilibria considerations proposed by Rogers is to circulate the spent water-gas, together with the steam that it contains, back to the water-gas generators where it is used in place of steam. The  $\text{CO}_2$  in the spent gas is reduced to  $\text{CO}$  and the steam to hydrogen. A purge from this closed circulating system is necessary to remove  $\text{CO}$  or  $\text{CO}_2$  produced from coke gasified in the generator, and also the nitrogen inevitably introduced. Nevertheless an improvement on the ordinary open cycle is claimed. Other workers suggest the condensation of steam and removal of  $\text{CO}_2$  from the spent gas before returning it to the retort.

The cycle usually claimed as most efficient is 20 minutes reducing and 10 minutes steaming, and there is a short purge after reducing before the hydrogen is turned to the collecting main. It is necessary periodically to burn out deposits of carbon from the iron mass, and if unpurified water-gas is employed, of sulphur as well. Carbon results from the decomposition of  $\text{CO}$  thus:



and is avoided or minimised by a high  $\text{CO}_2$  content of the water-gas, driving the above reaction from right to left. The same effect may be obtained by the addition of small amounts of steam to the inlet water-gas, which will produce  $\text{CO}_2$  by the "water-gas" reaction. However, since  $\text{CO}_2$  and steam are the products of reduction of the iron mass, this method of preventing carbon deposition will slow down the rate of reduction, and its application is therefore limited.

The various proprietary plants operating the process differ chiefly in the methods of heating the iron mass. The simplest is the Lane process in which the iron ore is contained in vertical cast iron or mild steel retorts arranged in a heating furnace. A bench of such retorts is usually laid out in groups of retorts so that one group may be steaming while one or two groups are reducing. Thus hydrogen production from the

bench is continuous. The bench is heated by burning producer-gas or spent water-gas.

In the *Bamag* process the iron mass is heated indirectly by means of a recuperator (single-retort process). Water-gas is passed through the iron mass and the spent gas is burned with air before it passes to the recuperator. After reduction, the water-gas is shut off and steam is passed through the recuperator and through the reduced mass. There are suitable purge periods, and air for burning off carbon deposits is admitted every cycle.

The *Messerschmitt Process* (Fig. 9) combines direct heating with the use of a recuperator. The iron mass is contained in an annular space between two iron cylinders. Water-gas is burned at the base of the inner cylinder with a quantity of air very much less than that required for complete combustion. The hot gas passes up through the chequer-work, down through the iron mass, and is finally completely burnt in the outer chequer-

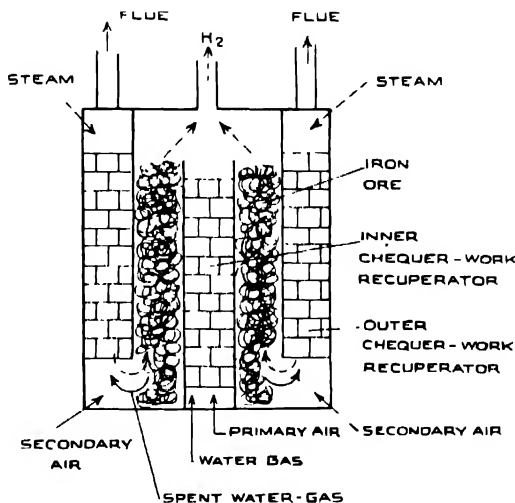


FIG. 9.

work. After 20 minutes reducing, the water-gas and air are shut off and steam is passed downwards through the outer recuperator where it is superheated, and upwards through the iron mass, hydrogen passing from the top of the retort. There is a short purge period.

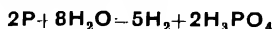
The crude hydrogen from an iron-steam plant will contain small quantities of  $\text{H}_2\text{S}$  (greater if the water-gas is unpurified),  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{N}_2$ . The  $\text{H}_2\text{S}$  may be removed by standard methods, and the  $\text{CO}_2$  by lime boxes. Final purities claimed are 90.5-99.75% (Lane process) and 98.5-99.5% (Messerschmitt).

Both multi- and single-retort processes have similar efficiencies (2 or 3 vol. water-gas per 1 vol. of  $\text{H}_2$ ). The costs of retort renewal in the multi-retort process may be heavy, and it has the disadvantage of a large number of hot joints. In a single-retort plant the volumes requiring purging are greater, and gas purities may be expected to be less than with a multi-

retort plant. This is borne out by the figures quoted above.

This process is not used to anything like the extent of the *Water-gas catalytic, electrolytic or Linde processes*. For the specific production of hydrogen for fat hardening it appears to have been replaced by electrolytic hydrogen. There have been no marked advances in industrial plant for a number of years.

**The Liljenrot Process.**—In this process, developed largely by the I.G., phosphorus is the intermediary when reducing steam. Thus elemental phosphorus is produced by reduction of pentoxide by carbon in the normal manner, and this reacts with steam thus:



The reaction is carried out in the presence of a catalyst and improvements in the catalyst have enabled operating temperatures to be reduced from 1,000°C. to 350–400°C. Apparently the

principal technical difficulty in operating this process is to avoid the production of phosphine and phosphorous acid, and two stages are apparently necessary.

The process was originally developed to allow synthesis of ammonia from the hydrogen obtained. This was to be neutralised with the phosphoric acid to give ammonium phosphate, a dual-purpose fertiliser. No large-scale installations of this process, however, have been reported.

**The Silicol Process.**—Here the intermediary is silicon or ferro-silicon. The silicon reacts with alkalis according to the following equation:



In practice less than the theoretical quantity of alkali is required. Where ferro-silicon is employed, the hydrogen yield only approaches theoretical when the silicon content is 80–90%. The process is exothermic and maintains itself at

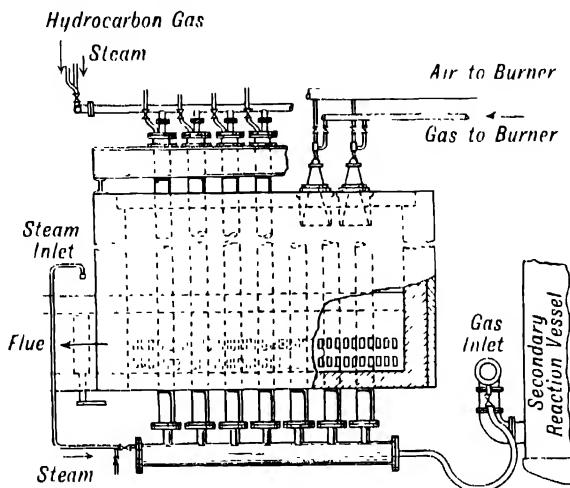
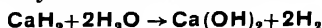


FIG. 10.

operating temperature. Careful control of admission of ferro-silicon is required to give the best results and to avoid carry-over of froth from the reaction vessel.

The process was originally developed during 1914–18 for producing hydrogen in the field or aboard ship for lighter-than-air craft. For this purpose the disadvantage of expensive raw materials was more than counterbalanced by the following advantages: a simple plant with low labour and power requirements, hydrogen rapidly produced and reasonably pure, with raw materials not excessively heavy or bulky. The only recent developments appear to be the generation of hydrogen under pressure by this process, and the development of a dry reaction by introducing water in crystalline compounds as, for example, gypsum.

**The Hydrolith Process.**—This was developed for the same purposes as the *Silicol* process. Calcium hydride reacts with water, thus:



Commercial calcium hydride yields upwards of 34,000 cu. ft. of hydrogen per ton. The reaction is markedly exothermic. Traces of nitride in the hydride lead to the production of ammonia which must be removed by water-scrubbing. The process is no longer used extensively.

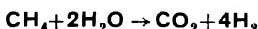
**Literature.**—For reaction equilibria in the iron-steam process, see p. 310d, also Taylor, "Industrial Hydrogen," Chem. Cat. Co. U.S.A., 1921, p. 25. Recent patents are Rogers, B.P. 249925 and 251124. For the *Silicol* and *Hydrolith* processes, see Teed, "Chemistry and Manufacture of Hydrogen," Edward Arnold, 1921, pp. 45, 67; also Jaubert, Compt. rend. 17th Congr. Chim. ind. Paris, 1937, 1130. For the *Liljenrot* Process, see G.P. 406411, 409344, 485068; B.P. 324122, 325533.

#### (4) REDUCTION OF STEAM BY HYDROCARBONS.

Gaseous hydrocarbons here replace coal in the extended form of the water-gas catalytic



process already described. The hydrogen in the hydrocarbons is usefully recovered, and the process can be written thus :



The reaction is usually carried out in two stages, approximately thus :

- (a)  $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$ ;  $\Delta H = + 51.6$  kg. cal. per g. mol. (endothermic).  
 (b)  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ;  $\Delta H = - 10.1$  kg. cal. per g. mol. (exothermic).

Stage (b) is exactly similar to the second stage of the water-gas catalytic process already described.

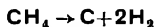
Since the total reaction is endothermic, the higher the temperatures the lower the equilibrium percentage of hydrocarbon. The reaction is therefore carried out at temperatures above about  $700^\circ\text{C}$ ., over a catalyst which may be contained in tubes of special steel which retains its strength at high temperatures. A typical composition for this steel is Cr 24, Ni 20, Mn 0.7, Si 1.0, C 0.22%. The tubes are contained in a brickwork furnace and are externally heated by combustion of fuel gas. There is a very extensive patent literature covering catalysts for this process. Fe, Ni, Ca promoted with Cr, V, Ce and K, Mg or Al have all been proposed.

The Standard Oil Company's plant at Bayway, N.J., U.S.A., has a capacity of 300,000 cu. ft. per hr. of hydrogen, and operates on refinery gases at atmospheric pressures and temperatures up to  $1,000^\circ\text{C}$ . There is less than 1% unconverted hydrocarbons in the exit gas.

*Literature.*—Ind. Eng. Chem. News Edition, 1932, 10, 205, describes the Bayway plant. Petroleum Zeitschrift, 1932, 28, 10 (Standard I.G.) describes an improved type of apparatus from which Figs. 10 and 11 are taken.

#### (5) CRACKING OF HYDROCARBONS.

Previous to the development of steam reduction by hydrocarbons, there was considerable activity in the development of processes for the production of hydrogen by the cracking of hydrocarbons thus :



The commercial success of any such process appears to depend largely on the value of the carbon black produced. There is only one large plant reported as operating on hydrogen obtained in this manner, that of the Shell Company in California. The methane-steam process has now clearly superseded cracking where hydrogen production is the sole consideration. It should be noted, however, that there is very considerable development now taking place in the petroleum industry in the direction of catalytic dehydrogenation of hydrocarbons. These promise to yield substantial quantities of fairly pure by-product hydrogen, and although no extensive use has yet been made of this source, it may become of considerable commercial importance.

During 1914-18 the Carbonian Gesellschaft developed a process for hydrogen production

from acetylene by decomposing with an electric spark at 2 atm. pressure. A number of Zeppelins were actually filled with gas thus produced, but the process is now no longer used.

*Literature.*—The Plant of the Shell Chemical Co., California, has been described by Rosenstein, Chem. Met. Eng. 1931, 38, 636.

#### (6) RECOVERY FROM COMMERCIAL GASES BY PARTIAL LIQUEFACTION.

Gases such as coke-oven gas and water-gas contain considerable quantities of  $\text{H}_2$  which may be separated from the remaining constituents by the physical process of partial liquefaction. Two main processes were developed

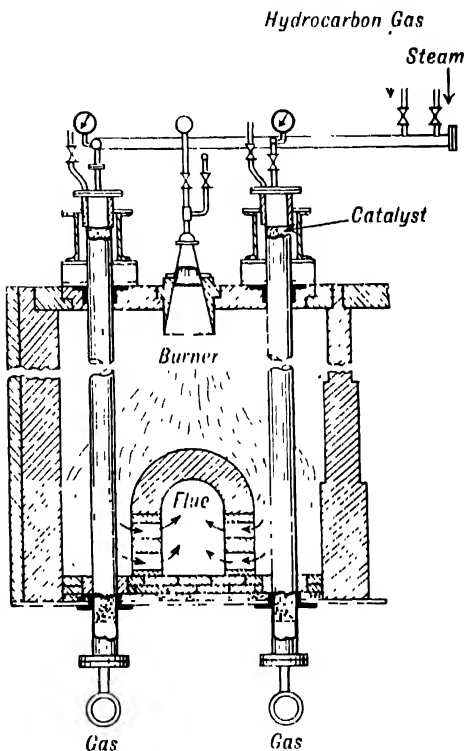


FIG. 11.

from about 1912 onwards, by George Claude in France, and by Linde and Bronn in Germany. The original main difference between these processes was the method adopted for obtaining the necessary low temperature. Claude used expansion of a compressed gas through a specially developed engine, which because of the low temperatures employed was lubricated with liquid nitrogen. Linde and Bronn used the Joule-Thomson effect by expansion through a porous plug, in actual practice an expansion valve. The following is a description of the Linde process as applied to coke-oven gas, which is the commonest case found industrially. It is significant that a number of plants originally obtaining hydrogen by the partial liquefaction

of water-gas have changed over to the *Badische* process.

The coke-oven gas is first purified from  $H_2S$ , usually by passage through iron-oxide boxes in the standard manner. It is then compressed to 10–12 atm. and is cooled with anhydrous ammonia to about  $-45^\circ C$ , a suitable cold exchanger being provided to economise power. This preliminary cooling effects the separation of water, followed by benzol and relatively high boiling substances. After warming in the cold-exchanger of the benzol removal plant, the compressed gas is scrubbed with water to remove  $CO_2$  and acetylene, and finally complete removal of  $CO_2$  is obtained by scrubbing with caustic soda solution. The compressed gas is then cooled by cold exchange with gases coming from a colder part of the system, then by anhydrous ammonia, and by further cold exchange until at a temperature of  $-145^\circ C$ , a fraction condenses out which contains practically all the  $C_2H_4$  and some  $CH_4$ . The ethylene in this fraction may

to  $-190^\circ C$ . with the liquid which has been expanded to a lower pressure (Fig. 12).

The very greatest care is taken to utilise all available cold and the latent heat of the condensed fractions, etc., so that all gases pass from the system at substantially room temperature. The  $3H_2 + N_2$  mixture, which is very pure, leaves at about 10 atm. pressure. Thus all the energy required for supplying cold to the system is provided by the evaporation of anhydrous ammonia, and the Joule-Thomson expansion of compressed cooled  $N_2$ . It is usual to mix the  $C_2H_4$ , the  $CH_4$  and the  $CO$  fractions (the latter containing considerable quantities of  $N_2$ ), and to return them as a heating gas of high calorific value to the coke ovens whence the original supply of coke-oven gas was obtained.

Plants for the partial liquefaction of coke-oven gas have also been built by Messer, and are apparently somewhat similar in operation to *Linde* plants.

*Literature.*—Borchardt, Gas- u. Wasser-fach, 1927, 70, 562, gives description of *Linde* process, analyses of gas fractions and estimated operating costs. See also Borchardt, Chem.-Ztg. 1930, 54, 649. For *Claude* process, U.S.P. 1135355, 1212455; Claude, Z. angew. Chem. 1930, 43, 417. For *Messer* plant, Van Iterson, Ingenieur (Holland), 1932, A, 47, 427, also Berthelot, Génie Civil, 1936, 108, 573.

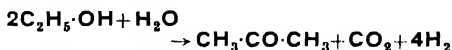
#### (7) PRODUCTION OF BY-PRODUCT HYDROGEN.

In the process of electrolysis of brine to produce caustic soda, a substantial quantity of hydrogen is obtained as a by-product, and in many cases this is recovered and utilised.

In the *Fernbach* or *Weizmann* process for the production of acetone and butyl alcohol by the fermentation of maize, a gas is given off which contains about 40%  $H_2$  and 60%  $CO_2$ . At one plant in the U.S.A. this gas is freed from alcohol vapour by active charcoal, and compressed and scrubbed with water until the  $CO_2$  content is 25%. The gas is then used to synthesise methanol.



The *Hig* process, which is used fairly extensively for the production of acetone from alcohol, gives by-product hydrogen by the following reaction:



*Literature.*—By-product hydrogen from *Fernbach* process, Anon., Chem. Met. Eng. 1930, 37, 548. Bakonyi, Chem.-Ztg. 1926, 50, 257. Woodruff, Ind. Eng. Chem. 1927, 19, 1147. See also Vol. V, 44a.

#### COSTS OF COMMERCIAL PRODUCTION.

be separated from the methane by further rectification, should it be required for other chemical processes. The temperature of the gas thus freed from  $C_2H_4$  is further reduced by cold exchange, and final cooling is by liquid  $N_2$  at  $-193^\circ C$ . when practically all the methane condenses out. In the last stage of purification the gas is washed counter-currently at 10 atm. pressure and  $-190^\circ C$ . with liquid nitrogen, which dissolves out the  $CO$  and at the same time partly evaporates to give the  $3H_2 + N_2$  mixture required for ammonia synthesis. To obtain the liquid  $N_2$ , pure compressed  $N_2$  from an air fractionation plant is supplied at about 110 atm. pressure. This is cooled by anhydrous ammonia and then by cold exchange to about  $-180^\circ C$ . Finally it is let down through an expansion valve when cooling by the Joule-Thomson effect causes liquefaction at  $-193^\circ C$ . The  $N_2$  which evaporates is warmed by cooling the inlet gases and passes from the system for recompression. That portion of the liquid  $N_2$  required to scrub out  $CO$  is let down to 10 atm. only and cooled

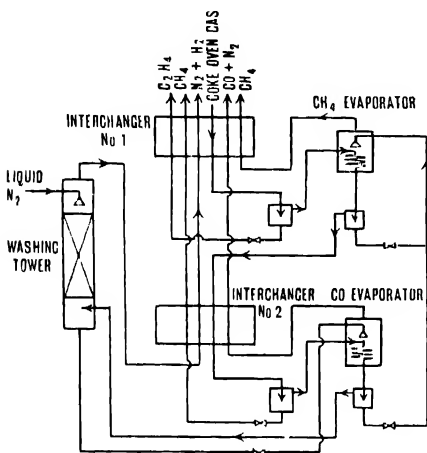


Fig. 12.

It is difficult to give generalisations on the relative costs of hydrogen by the processes already described, because the cheapest process for any particular requirement will depend on a number of circumstances, and each individual case must be considered on its merits. This is clear from the fact that the various processes

already described do actually operate in commercial competition. If any one process were overwhelmingly cheaper under all conditions, it would supplant all others. Clearly the main factors affecting the choice of process will be (a) the raw materials available, (b) the cost of power, (c) the purpose for which the hydrogen is to be used, (d) the quantity required. Taking these factors in turn, the following examples are illustrative:

(a) Where brown coals or lignite are available and coke is expensive, one of the coal-gasification processes worked in conjunction with the *Badische* process, as described above, is likely to be favoured. Thus in Germany the I.G. use the *Winkler* process extensively, and there are *Didier* plants producing *Fischer* synthesis-gas (see later). In Hungary the ammonia plant at *Petfurdo* has a *Didier* plant operating on lignite. Where large quantities of surplus coke-oven gas are available, e.g. in Belgium and Holland, the partial liquefaction processes (*Claude*, *Linde* or *Messer*) are widely employed. At oil wells, refineries, and coal- or oil-hydrogenation plants the availability of surplus hydrocarbon gases has favoured reduction of steam with these gases to produce all or part of the hydrogen required for hydrogenation.

(b) Ample and cheap electric power will favour the *electrolytic* process. Thus Norway has a large synthetic ammonia plant operating on electrolytic hydrogen from hydro-electric power, and this method was proposed in recent schemes for harnessing the *Aswan Dam* in Egypt. However, to be economically attractive in competition with the *water-gas catalytic* or *partial liquefaction* processes, the power must be very cheap indeed. *Pollitt* has shown that with power at 0.07d. per kw.h., electrolytic hydrogen will compete with other processes. The high capital cost of electrolytic and ammonia-synthesis plant precludes the erection of plant operating only on off-peak or seasonal power.

(c) For reasons already given,  $\text{CH}_4$  is objectionable in gases to be used for ammonia synthesis. This consideration will militate against the use of the coal-gasification processes, or steam reduction with hydrocarbons, except in cases where the decomposition of  $\text{CH}_4$  is very complete. For *Fischer* synthesis the necessity for a very low  $\text{CH}_4$  content does not hold, and thus coal-gasification processes are frequently employed. For fat-hydrogenation extreme purity is essential, hence electrolytic hydrogen is favoured.

(d) The largest synthetic-ammonia plants operate on coke by some form of the *water-gas catalytic* process. Two factors can explain this: (1) Coke is usually available in larger quantities than say coke-oven gas. Where the latter is used, the amount of hydrogen which can be made is regulated by the output of the coke ovens, in its turn depending on the market for coke. Thus an absolutely assured supply of gas may be difficult to obtain. (2) The *water-gas catalytic* process is more easily adapted for large-scale production than most of the other processes. A large number of the smaller synthetic-ammonia plants use *partial liquefaction* of coke-oven gas to supply hydrogen, but the

major factor in deciding this is probably (a) above. There is no reason to suppose that this process is particularly adapted to small and intermediate hydrogen outputs. For very small outputs such as those required for the hydrogenation of fats, and where the hydrogen cost is not a big factor in the total cost of the product, the *electrolytic* or *iron-steam* processes may be employed in spite of their high operating costs.

One estimate of the relative importance of the various processes gives the percentages of the world's total hydrogen production as follows: *Water-gas catalytic* and related processes 55%, *partial liquefaction* 26%, *electrolysis* 16%, all other methods 3%.

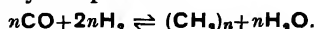
*Literature*.—For a comparison of electrolytic and *water-gas catalytic* processes, see *Pollitt*, *Trans. 2nd World Power Conference*, Berlin, 1931, 2, 145. For estimated cost of stages of the *water-gas catalytic* process, see *Laupichler*, *Chem. Met. Eng.* 1936, 43, 122, and *Gas World*, 1936, 105, 71. For cost of electrolytic hydrogen, *Zdansky*, *Chem. Fabrik*, 1933, 49, and of *Linde* process, *Borchardt*, *Gas- u. Wasserfach*, 1927, 23, 1, and *Metallborse*, 1930, 20, 1856. For cost of *Fischer* synthesis gas by a number of processes, see *Schultes*, *Gluckauf*, 1936, 72, 273.

#### TECHNICAL USES.

The relative importance of the various commercial uses for hydrogen may be illustrated by the following figures applying to the U.S.A. for 1938. Of a total consumption of about  $25 \times 10^9$  cu. ft., approximately 66% went to ammonia synthesis, 19% to synthetic methanol, 9% to technical *isooctane*, and 6% to petroleum hydrogenation. No data are available for Europe, but the relative orders of importance would probably be (1) Ammonia production, (2) Motor fuel production including hydrogenation, (3) Synthetic alcohols production, (4) Other uses.

(1) *Synthetic Ammonia* (see AMMONIA, Vol. I, 331d).—The sources of the hydrogen used in world production of synthetic ammonia are approximately as follows: *Water-gas catalytic* 52.4%; *partial liquefaction* coke-oven gas 21.1%; *electrolysis* of water 17.0%; other processes 1.5%.

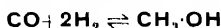
(2) *Motor Fuels* (see HYDROGENATION OF COAL).—This represents one of the most recent developments in the commercial use of hydrogen. It includes hydrogenation of bituminous and brown coals, coal distillation products, petroleum and petroleum residues, and hydrocarbon synthesis by the *Fischer-Tropsch* process which may be represented:



There are a number of *Fischer-Tropsch* and brown coal hydrogenation plants in Germany. In England the I.C.I. plant at *Billingham*, Co. Durham, hydrogenates bituminous coal and creosote oil. In Italy there are plants hydrogenating Albanian crude oil and petroleum residues. In America plants at *Baton Rouge* (Louisiana) and *Bayway* (N.J.) have been used for hydrogenation of gas oils and for the production of special types of lubricants by hydrogenation. A recent development is the production of the high-efficiency aviation fuel *iso-*

octane by the hydrogenation of *isooctene*. Since in petroleum refineries there are usually available considerable quantities of surplus hydrocarbon gases, these are generally used to reduce steam for the production of hydrogen.

(3) **Synthetic Organic Chemicals** (*see CATALYSIS*, Vol. II, 425c).—The most important product in this class is undoubtedly methyl alcohol or methanol produced by the reaction:



Recently there has been considerable expansion in the synthesis of higher alcohols by analogous processes. Water-gas partly converted with steam to give the required  $\text{H}_2\text{:CO}$  ratio is the commonest starting material, but coke-oven gas partly burnt with air has also been proposed. The gases remaining after passage through a methanol converter are then used for the synthesis of ammonia.

(4) **Fat Hardening** (*see HARDENED OR HYDROGENATED FATTY OILS*).

(5) **Lighter-than-Air Craft**.—The development of the airship has been impeded by a number of serious accidents and by the perfection of the aeroplane. Nevertheless for a number of specialised purposes lighter-than-air craft are still used. For instance, protection of objectives from attacking aircraft is secured by a number of balloons moored by cables (the balloon barrage). The hydrogen is then required in comparatively small quantities over widely distributed areas, and the development of relatively light-alloy steel cylinders has clearly helped considerably in the solution of this problem. The Graf Zeppelin Co. used small electrolytic hydrogen plants at its various bases for replacement of the hydrogen losses.

(6) **Heating and Welding**.—The intense heat of the oxygen-hydrogen flame enables it to be used for autogenous welding and the flame-cutting of steel plate. For this reason also, it was once employed for producing an intense light for cinema lanterns, etc., by heating lime to incandescence. The development of the electric arc and special forms of filament lamp has completely superseded "limelight," and for welding, acetylene is generally preferred because it is easier to generate in small quantities, is easily stored under pressure in acetone (dissolved acetylene) and the oxy-acetylene flame is hotter (*see ACETYLENE, ITS USE IN INDUSTRY*, Vol. I, 111). For some purposes, however, the carbon in acetylene is objectionable, and for welding of aluminium on platinum, for the fusion of quartz to give artificial gems, and for certain cutting operations the oxy-hydrogen flame is still employed (*see GEMS, ARTIFICIAL*).

In welding with the electric arc, hydrogen has two uses. It can be used to shield the arc, thus preventing the formation of oxides or nitrides of iron, or by passing hydrogen through an arc formed between two tungsten electrodes, it can be dissociated to atomic hydrogen. Molecular hydrogen re-forms 6–10 mm. from the arc with evolution of intense heat. An alternating current arc is usually employed, and the temperature thus obtained is probably above 3,760°C. The development of covered electrodes for ordinary electric-arc welding has prevented any

great extension of the use of hydrogen for shielding welding work from atmospheric attack, but for certain specialised purposes, *e.g.* the welding of thin sections, atomic-hydrogen welding is still fairly extensively employed.

(7) **Bright Annealing**.—Metallic objects may be annealed in an atmosphere of nitrogen or hydrogen or mixtures of these gases, when it is desired to avoid the formation of an oxide scale which must otherwise be removed by "pickling" in the usual manner. This process is termed "bright annealing" and it may actually be extended to de-scaling, but in such cases the finely divided metal on the surface of the object treated gives a matt and not a burnished finish. A good example of bright annealing is in the production of motor-car lamp reflectors. The brass pressing is so deep that it must be done in stages, and bright annealing is carried out between each stage. When using hydrogen for the bright annealing of steel parts, decarburisation of the surface may result. If this is objectionable it can be prevented by the introduction of a suitable quantity of hydrocarbons into the reducing atmosphere.

(8) **The Production of Metals**.—Hydrogen is extensively used for the reduction of metallic oxides, *e.g.* in the production and working of tungsten and molybdenum. It can also be used in the production of metallic magnesium by reduction of the oxide with carbon. If the CO and magnesium vapours issuing from the reduction furnace are cooled slowly, the reverse reaction to that taking place in the furnace will occur, resulting in the production of carbon and magnesium oxide. This can be prevented by rapidly chilling the gases issuing from the furnace with a blast of cold hydrogen.

**Literature**.—Synthesis of alcohols, Natta, *Österr. Chem.-Ztg.* 1937, **40**, 162. Atomic hydrogen welding, Weinman and Langmuir, *Gen. Electric Review*, 1926, **29**, 160; Miller and Deglon, *Sheet Metal Industries*, 1934, **8**, 131, 189, 252; Guest, *Metal Treatment*, 1936, **2**, 17.

## TECHNIQUE AND TRANSPORT.

**Hydrogen Attack on Steel**.—Compressed hydrogen can cause fissuring and a severe reduction of the tensile strength and impact value of steel. Under some conditions this may occur at relatively low temperatures, *e.g.* 150–200°C. The effect is due mainly to decarburisation, but in some cases deterioration of the properties of the steel takes place before decarburisation and the effect is then due to hydrogen adsorption. In general nickel-chromium-molybdenum steel alloys are more resistant to attack than mild steel, but in all cases careful heat treatment is required to obtain the best service.

**Literature**.—Ingles and Andrews, *J. Iron and Steel Inst.* 1933, **127**, 2, 383. Baukloh and Guthmann, *Z. Metallk.* 1936, **28**, 34, describes also the effect of hydrogen on Cu, Ni and Al.

**Hydrogen Transport**.—During the last few years the difficulties of transport of all compressed gases, including hydrogen, have been to some extent reduced by the development of relatively light cylinders of special alloy steels. One very convenient form in which hydrogen

may be transported is as liquid ammonia. Passage of ammonia gas at low pressures over catalysts similar in type to those used for the ammonia-synthesis reaction and operating at about 400°C. results in practically complete (99.5%) decomposition to  $N_2 + 3H_2$ . The space velocity employed is about 500 cubic metres of gas per hour per cubic metre of catalyst. A 100 lb. cylinder of anhydrous ammonia contains the equivalent of 3,400 cu. ft. of hydrogen, and for a large number of purposes, e.g. bright annealing, the presence of 25% nitrogen in the hydrogen obtained is of no serious consequence. The apparatus for decomposing the ammonia is usually termed an "ammonia cracker." "Cracked" methanol, which is a 2:1 mixture of hydrogen and carbon monoxide, can also be used for a number of purposes, although the presence of carbon monoxide limits its applications as compared with "cracked" ammonia.

Suggestions have been made to transport hydrogen as a liquid at 1 atm. absolute pressure in heat-insulated containers. Liquid oxygen is transported by such methods, but liquid hydrogen in comparison has a number of very serious disadvantages. The temperature is  $-253^\circ\text{C}.$ , the specific gravity only 0.07, and problems of transport are complicated by the continuous evolution of an inflammable gas, due to heat leaks into the container, and the exothermic change from ortho- to para-hydrogen which takes place at low temperatures.

*Literature.*—Ammonia Crackers, B.P.473696.

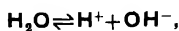
H. S. C. and P. H. S.

**HYDROGEN ION DETERMINATION.** The relative acidity of an aqueous solution is the most important single factor determining its properties and reactions. This "acidity" is measured by the concentration of hydrogen ions in the solution and, since this quantity may vary over a very wide range, it is convenient to express it on a logarithmic scale. The convention, that is now always followed, was introduced by Sorensen (1909) who used the term  $p_H$  and defined it by the following expression:

$$p_H = \log_{10} \frac{1}{[H^+]} \quad \text{or} \quad p_H = -\log_{10} [H^+]$$

where  $[H^+]$  is the hydrogen ion concentration of the solution. It is now known that these ions are hydrated and they would be written more correctly as  $H_3O^+$ , but as it is still customary to represent them as  $H^+$  this simpler practice will be followed.

A perfectly pure sample of water will be neutral but it still has some electrical conductivity, indicating that there are charged particles (ions) in solution. In this case they are hydrogen and hydroxyl ions, formed by the dissociation of the water,



and they must be present in equal concentrations. If by any means the hydrogen ion concentration is made larger than that of the hydroxyl the solution is said to be acid while, if the converse is the case, the solution becomes more alkaline as the excess of hydroxyl ions increases. The electrolytic dissociation theory

indicates that the product of the concentrations of these two ions is a constant which is known as the ionic product for water. This quantity has been measured and at  $25^\circ\text{C}.$  is equal to

$$1.42 \times 10^{-14}$$

when concentrations are given in gram ions per litre. The quantity changes with temperature and at  $22^\circ\text{C}.$  is equal to

$$1.01 \times 10^{-14}$$

and at room temperature the following expression is nearly correct:

$$[H^+][OH^-] = 10^{-14}$$

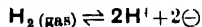
If the hydroxyl ion concentration is measured on the logarithmic scale, defining  $p_{OH}$  in a fashion analogous to  $p_H$ , one can write

$$\log_{10} [H^+] + \log_{10} [OH^-] = -14 \quad \log_{10} 10 = -14$$

$$\text{or} \quad p_H + p_{OH} = -14$$

Hence the acidity or alkalinity of any aqueous solution can be expressed in terms of either  $p_H$  or  $p_{OH}$ ; if the  $p_H$  is greater than seven the solution is alkaline and if smaller it is acid. The measurement and control of the above quantities are important whenever an aqueous solution is used and it is therefore not surprising that  $p_H$  measurements are employed in the most diverse types of industrial processes, among which are the refining of sugar, the manufacture of sweets, the tanning industry, brewing, medicine, bacteriology and the preparation of pharmaceutical products.

The *Hydrogen Electrode* is the ultimate standard to which all determinations of  $p_H$  are referred. Finely divided platinum or iridium is able to act as a catalyst by means of which hydrogen gas can be converted reversibly into hydrogen ions, according to the equation



and when a plate, covered with platinum black, is lowered into a solution that has hydrogen gas above it the above reaction will tend to take place. The metal plate will take up the free charge, indicated by  $\ominus$ , until the electric potential between the plate and the solution has built up so as to prevent further change. This potential is a measure of the tendency of the hydrogen gas to split up into ions and pass into the given solution, and any practical apparatus for this measurement can be called a hydrogen electrode. It can be shown that, if the hydrogen gas is at one atmosphere and the potential of the electrode is  $E$  volts, the following relationship holds:

$$E = -\frac{RT}{F} \log_e [H^+]$$

where  $T$  is the absolute temperature,  $F$  the Faraday and  $R$  the gas constant. Or at  $18^\circ\text{C}.$

$$E = -0.058 \log_{10} [H^+], \text{ i.e. } p_H = \frac{E}{0.058}$$

In order to measure the potential between the platinum plate and the solution the latter must be connected to the measuring instrument. This is done by means of another electrode system where there is a solid conductor in contact with a solution. A second potential difference is thus involved which must be as constant and

reproducible as possible in different apparatus. The calomel half-element is the device that is normally used, it consists of a layer of pure mercury connected with the potentiometer by a platinum wire fused through the bottom of the vessel. The mercury is covered with a solution of normal potassium chloride that has been saturated with mercurous chloride, the excess of which forms a thin layer on the surface of the metal. Provided that the calomel half-element has been set up with pure chemicals the E.M.F. between solution and mercury is +0.2816 volts at 25°C. with a temperature coefficient of  $-0.00024$  volts per °C. It is possible to make

up standard cells in a similar fashion with solutions that are respectively  $N/10$  or saturated with potassium chloride; the E.M.F.'s of these cells at 25°C. are +0.3341 and 0.2426 volts respectively and their temperature coefficients  $-0.00070$  and  $-0.00076$  volts per °C. (see Lewis, Brighton and Sebastian, *J. Amer. Chem. Soc.* 1917, 39, 2245; Randall and Young, *ibid.* 1928, 50, 989; D. A. MacInnes, "The Principles of Electrochemistry," Reinhold, New York, 1939, p. 247).

Contact between the potassium chloride solution and that around the hydrogen electrode is normally made through a  $\cap$ -shaped capillary or

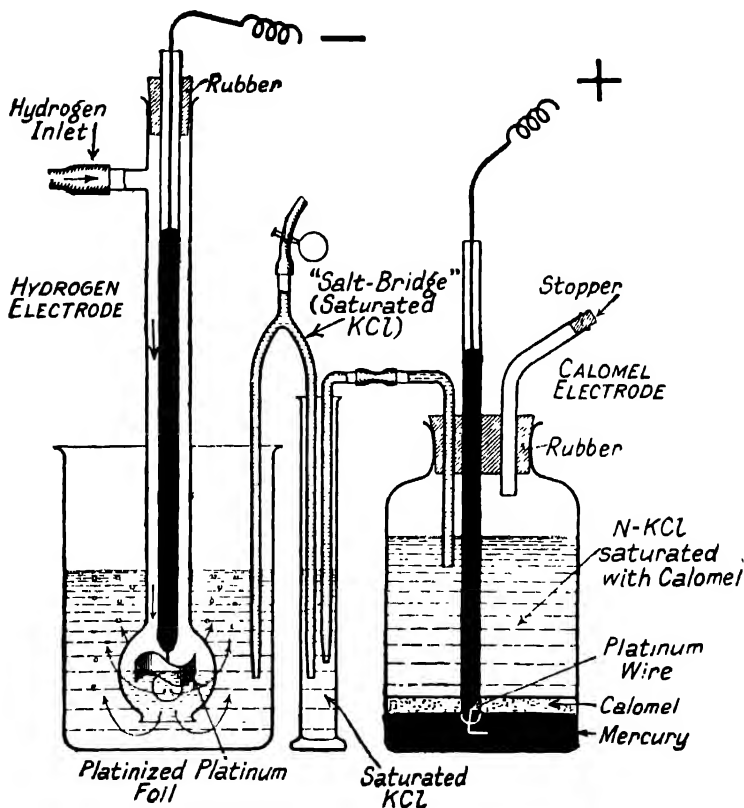


FIG. 1.

quill tubing "salt bridge" that is filled with either saturated potassium nitrate or saturated potassium chloride solution. A typical set up of a hydrogen electrode and calomel half-element is shown in fig. 1. The E.M.F. of the complete cell is measured with a potentiometer and a high resistance galvanometer using the usual Poggendorff method; the  $p_H$  of the solution around the hydrogen electrode is calculated from the following expression:

$$-\log_{10} [H^+] = p_H = \frac{\text{E.M.F. observed} - \text{E.M.F. calomel electrode}}{0.058}$$

The hydrogen electrode has certain limitations which restrict its use and may introduce errors. One of the most serious of these is the ease with which the platinum black adsorbs "poisons" which prevent it acting efficiently as a catalyst for the interchange of hydrogen ions and hydrogen gas. Arsenic, hydrogen sulphide, mercury and certain organic dyes are common materials producing this trouble, which manifests itself by abnormal values and by a tendency for the measured  $p_H$  to change erratically with time. A further difficulty is introduced by the possible interaction of the hydrogen, which is in an active condition on the platinum surface, with any

reducible substance in the surrounding solution. Strong oxidising agents, salts of easily reduced metals, or organic compounds will consequently interfere with the functioning of the electrode, and it should never be used in their presence. The  $p_H$  of such solutions may be found by one of the secondary methods: i.e. by a comparison of the unknown solution with one whose  $p_H$  is known from hydrogen electrode measurements.

*Colorimetric Methods* provide a very simple and convenient way of effecting this comparison. A suitable indicator is added to the solution and the colour compared with the shade that it assumes in a series of solutions whose  $p_H$  values are known. The simplest form of apparatus for this purpose is shown in fig. 2. It consists of a block of wood, or other suitable material, e.g. bakelite, in which six holes are bored so that test-tubes can be slipped into them. Slits are cut in the block through which the colour of the light that passes through each of the three pairs of tubes in the direction of the arrow can be compared.

The middle pair of tubes contain the solution to be tested with a little of the indicator added and plain water respectively. Each of the outer

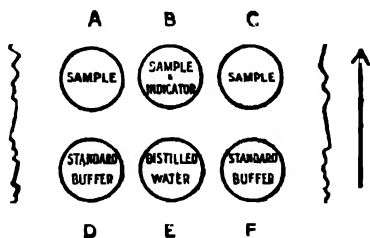


FIG. 2.

pairs of tubes contain respectively the test solution without indicator and a solution of known  $p_H$  containing an equal concentration of indicator. The tubes of known  $p_H$  are changed until the colours observed through the slots match, or if that is impossible, a slightly lighter colour is observed on one side of the test solution and a darker colour on the other. The  $p_H$  of the solution can then be said to be between those of the two standards and a visual estimate of its value can be made. The procedure described compensates for any colour in the test solution unless this is very strong, in which case the colorimetric method is not applicable.

Provided that the indicator and conditions are standardised it is possible to replace the tubes containing the indicator and standard solutions with coloured glass which is not subject to change and deterioration. A number of convenient types of apparatus, "comparators," are now on the market in which a series of glass discs are suitably mounted—generally in a ring so that one after the other is compared with the unknown solution until a match is obtained.

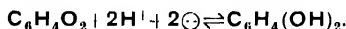
When solutions of known  $p_H$  have to be made up it is obviously desirable that their hydrogen ion concentrations shall be practically unchanged by the addition of other substances. For

example, they must change as little as possible owing to the absorption of alkali from a glass vessel, or carbon dioxide from the air. Solutions that have a reserve acidity or alkalinity so that the hydrogen ion concentration changes but slightly on dilution and on the addition of acids and alkalis are called "buffer solutions." They are generally made by mixing a weak acid or base with a solution of one of its salts, the effect of which is illustrated by the following figures. If 1 c.c. of normal hydrochloric acid is added to 100 c.c. of water the  $p_H$  changes from 7 to 2, i.e. 5 units. A 0.0256 molar potassium dihydrogen phosphate solution which is also 0.0411 molar with respect to disodium hydrogen phosphate also has a  $p_H$  of 7, but when 1 c.c. of normal acid is added to a corresponding volume the  $p_H$  is only reduced to 6.75.

A large number of buffer solutions are available, most of them covering a range of 2-3  $p_H$  units. Britton and Robinson (J.C.S. 1931, 1456), however, have described a "universal buffer solution" which works from  $p_H$  3.5 to 9. It is prepared by taking a  $N/35$  solution of hydrochloric acid and adding sufficient potassium dihydrogen phosphate, citric acid, boric acid and veronal so that when they are dissolved the solution is  $N/35$  with respect to the replaceable hydrogen of each of them. Then if  $x$  c.c. of pure carbon-dioxide-free  $N/2$  caustic soda solution is added to each 100 c.c. of the above solution the  $p_H$  of the resulting mixture is given by the expression  $p_H = 2.686 + 0.0853x$ . Provided the chemicals are pure these figures should be correct to 0.02 of a unit of  $p_H$ .

The colorimetric method has many advantages; it is rapid in action, uses only simple apparatus and can be readily adapted to specialised needs. For example, it can be used with very small quantities if the liquids to be compared are contained in capillary tubes. These advantages should not cause errors to which the method is subject to be overlooked. The indicator used has its own acidic properties and if the solution to be tested is not buffered its  $p_H$  may be changed appreciably when the indicator is added. This effect is called "the acid error"; and it may be eliminated by first making a rough determination and then buffering the indicator so that it is approximately isoelectric with the test solution. This mixture is then used for a more accurate determination of the  $p_H$ . Errors may also be introduced when certain other materials are present in the solution; these are commonly known as "salt" or "protein errors" and they may become very large indeed under unfavourable conditions. Thus a 0.01  $N$ -hydrochloric acid and 0.29  $N$ -potassium chloride solution has a  $p_H$  of 2.05, but the value determined with Methyl Violet is 1.91, with Methyl Green it is 1.82, while with Tropæoline OO it is 2.02. Similarly a dilute sulphuric acid solution containing egg albumin gave a  $p_H$  value of 2.49 with the hydrogen electrode, but colorimetrically it was 2.53 using Methyl Violet and of the order of 5.0 using Congo Red. The indicators recommended by the manufacturers to cover a given  $p_H$  range are normally those which give as small a salt and protein error as possible.

The *Quinhydrone Electrode* is the most common method of measuring  $p_H$  by a potentiometric procedure. The conditions for the use of the electrode were first worked out by E. Biilmann (Ann. Chim. 1921, [ix], 15, 109; 1921, [ix], 16, 321). Later the electrode was studied in detail by Livingstone, Morgan and collaborators (J. Amer. Chem. Soc. 1931, 53, 454, 597 and 2154, *idem*, *ibid.* 1932, 54, 910) who confirmed the earlier work showing that the electrode is quickly and easily prepared, develops its potential very quickly, is not affected by atmospheric pressure and, since it does not require a gas to be bubbled through the solution, can be used for work on body fluids containing carbon dioxide. To set up an electrode it is only necessary to immerse a bright platinum plate in the test solution, to which a little quinhydrone has been added, and then measure the E.M.F. between the plate and solution, employing a standard calomel half-element in an identical fashion to that used for the hydrogen electrode. It is best to have the platinum plate on a long length of platinum wire; if this is impossible and the wire is sealed through glass which is in contact with the solution great care must be taken that the seal is a perfect one or considerable error may be introduced. The electrode should be cleaned in boiling cleaning mixture, allowed to cool, washed in a stream of tap water, then in distilled water and after rinsing in alcohol allowed to dry. With ordinary laboratory apparatus satisfactory results are obtained with an electrode that is 1 cm. square or larger. The electromotive force  $E$  taken up by the platinum with respect to the solution will be determined by the following equation.



The concentrations of quinone and hydroquinone are the same, since they are introduced as the molecular compound quinhydrone and the only other variables are the hydrogen ion concentration and the tendency of the solution to give up electrons. Consequently  $E$  should be a function of the hydrogen ion concentration and it is found that

$$\text{at } 20^\circ\text{C.} \quad E = 0.7044 + 0.0581 \log_{10}[H^+]$$

$$\text{and at } 25^\circ\text{C.} \quad E = 0.6994 + 0.0591 \log_{10}[H^+]$$

For precision work a saturated solution of the quinhydrone is employed but in works control, where there is a continuous recording of  $p_H$  and costs become important, it is possible to reduce the concentration to 1 part in 10,000 and still obtain an accuracy of  $\pm 0.05$   $p_H$  units (C. C. Coons, Ind. Eng. Chem. [Anal.], 1931, 3, 402).

The chief disadvantage of the quinhydrone electrode is that it is unsuitable for use above  $p_H$  8.5, where the acid character of the hydroquinone begins to manifest itself and hence there is a tendency for it to react with the solution; the atmospheric oxygen also begins to attack the quinhydrone at about this  $p_H$  value.

The errors introduced by salts have been studied by Biilmann (*l.c.*) and also by Hovorka and Dearing (J. Amer. Chem. Soc. 1935, 57, 446).

The magnitude of the errors to be anticipated are shown by the following figures:

Salt concentration.		Error in $p_H$ measured by the quinhydrone electrode.
	<i>N</i>	unit of $p_H$
NaCl . . .	0.4	-0.02
KCl . . .	2.0	-0.09
MgSO <sub>4</sub> . . .	1.0	+0.02
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . . .	0.5	+0.019
" . . .	1.0	+0.038
" . . .	2.0	+0.078

It will be seen that the results for ammonium sulphate indicate that the error is nearly proportional to the salt concentration. This relationship was also found with the errors introduced by other salts. If the concentration is not large the salt and protein error can be neglected for most practical purposes.

The *Glass Electrode* has in recent years found increasing use, especially in physiology and biochemistry. Its popularity is due to the production of suitable electrodes and measuring instruments as standard commercial articles. Earlier work was hampered by the difficulty of E.M.F. measurements through the high resistance of a glass diaphragm, but this has been overcome by the use of special glasses that have a minimum electrical resistance and by the cheap production of wireless valves that can be made to work as voltmeters even when the external resistance is high—a hundred megohms or more. It must be realised that there is no satisfactory theoretical relationship between a glass electrode and a solution of given  $p_H$ , but that it does serve as a method of comparing a series of solutions. In practice the electrode is standardised against a known buffer whose  $p_H$  is as near as possible to that of the unknown solution.

The most common form of glass electrode is a thin-walled bulb a few centimetres in diameter which contains an acid solution saturated with quinhydrone into which a platinum wire is dipping. The tube is generally sealed off and consequently the external lead is connected to one side of the glass diaphragm under constant conditions. This bulb is then dipped into the test solution and the circuit completed with a calomel half element in the usual manner. It is then found that the E.M.F. of the bulb with reference to the solution varies with its hydrogen ion concentration in the  $p_H$  range of 2-8 units and can be represented by the familiar type of formula in which  $E_0$  is the E.M.F. that the electrode would take up in a solution that is normal with respect to hydrogen ions and  $k$  is a constant.

$$E = E_0 - k \log_{10}[H^+]$$

i.e.

$$p_H = \frac{E - E_0}{k}$$

The most suitable glass available for the construction of electrodes contains 72% SiO<sub>2</sub>, 22% Na<sub>2</sub>O and 6% CaO and is known commercially as Corning 015 glass (see Hughes J.C.S.



1928, 491; Dole *et al.*, J. Amer. Chem. Soc. 1930, 52, 29; Trans. Electrochem. Soc. 1937, 72, 129; Gardiner and Sanders, Ind. Eng. Chem. [Anal.], 1937, 9, 274).

Even when the glass electrode is properly made it is necessary to watch for irregularities that may be introduced by dissolved salts and organic materials. Considerable work has been carried out to find the conditions under which these errors become pronounced. In general it may be said that the greater the salt concentration the lower the  $p_H$  at which the electrode will function satisfactorily. For example, in the presence of 0.1N-sodium chloride the electrode is satisfactory up to  $p_H$  10.5, but with a normal solution the errors become serious at above  $p_H$  8.5. See Gardiner and Sanders (*l.c.*).

As the temperature is increased the difficulties in using a glass electrode are greatly increased. The deviations become very much larger, also the readings obtained are not consistent and consequently, unless special precautions are taken, the glass electrode should not be used above 30°C. A further difficulty is that the glass used is of the soft variety and, if the test solution is unbuffered, sufficient alkali may be taken from the glass to effect a considerable change in the  $p_H$  (see Humphreys, Chem. and Ind. 1939, 58, 281). In spite of its errors the glass electrode provides a very convenient mechanism for investigating the  $p_H$  of solutions where other methods are impossible. It is not affected by oxidising or reducing agents, it does not introduce salts or other obnoxious materials into the specimen to be tested and the electrode does not deteriorate with time; moreover the  $p_H$  range 5-7 in which the electrode functions best is the one which includes most biological fluids. Hence it is not surprising that the electrode is much used especially where speed rather than extreme accuracy is required.

The *Antimony Electrode* is sometimes used when a rough comparison of the  $p_H$  of similar solutions is required. It consists of a rod of antimony covered with a superficial layer of oxide by atmospheric oxidation. It is claimed that greater uniformity is obtained if the metal is covered with a layer of sulphide (Ball, Schmidt and Bergstresser, Ind. Eng. Chem. 1934, 6, [Anal.], 60; Ball, Trans. Electrochem. Soc. 1937, 72, 235), the general conditions for its use have not been sufficiently worked out, and it is not recommended except when cheapness and simplicity are the all important factors.

**Bibliography.**—Britton, "Hydrogen Ions," Chapman and Hall, 1932; Clarke, "The Determination of Hydrogen Ions," 3rd ed., Williams and Wilkins, 1928; Jorgensen, "Die Bestimmung der Wasserstoffionen-konzentration und deren Bedeutung für Technik und Landwirtschaft," Theodor Steinkopff, Dresden, 1935; MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939.

R. H. P.

**HYDROGEN OVERPOTENTIAL** (*v.* Vol. III, 376b).

**HYDROGEN PEROXIDE.** *History.*—Hydrogen peroxide,  $H_2O_2$ , was discovered in 1818 by Thenard (Ann. Chim. Phys. 1818, [ii],

8, 306; 9, 51, 94, 314, 441) who obtained it by the action of acids on barium peroxide. Thenard found that the new substance behaved as "oxygenated water," and established its formula as  $H_2O_2$ . He also described many of its characteristic properties, including the decomposition by solid catalysts and by heat, and showed that as one of the oxygen atoms is only very loosely bound the compound is a powerful oxidising agent. At first hydrogen peroxide was obtained only in dilute aqueous solution, but it was later found possible to concentrate it by evaporation under reduced pressure, and in 1904 the firm of E. Merck (G.P. 152173) produced a concentrated solution free from solid residue by direct distillation of the solution resulting from the action of sulphuric acid on sodium peroxide. The important electrochemical method of preparation, based on the formation of persulphuric acid, was patented in 1907 (G.P. 217539). Substantially pure  $H_2O_2$  was first obtained by Wolfenstein in 1894 (Ber. 1894, 27, 3307), and in 1920 Maass and Hatcher (J. Amer. Chem. Soc. 1920, 42, 2548) starting with a 3% solution prepared pure hydrogen peroxide by fractional distillation and evaporation and finally by crystallisation.

*Natural Occurrence.*—Extremely minute quantities of  $H_2O_2$  are said to occur in the atmosphere and in natural waters. E. Schöne (Ber. 1874, 7, 1693; 1878, 11, 483, 561, 874, 1028) reported up to 1 mg.  $H_2O_2$  per litre in rain water, but only 0.05 mg. per litre in dew and hoar frost. The atmosphere was said to contain about  $4 \times 10^{-10}$  g.  $H_2O_2$  per litre. Schöne and others concluded that it is formed in the atmosphere by the action of sunlight. However, much of the early work on the natural occurrence of traces of  $H_2O_2$  is untrustworthy and lacks modern confirmation.

Similarly, early reports of the occurrence of  $H_2O_2$  in animal and vegetable tissues are unreliable. However, recent work has established beyond doubt the presence of  $H_2O_2$  in various biological systems. Working with lactic fermentation bacteria (which contain no catalase (*q.v.*)—the common enzyme which decomposes  $H_2O_2$ ) Bertho and Gluck (Naturwiss. 1931, 19, 88) claimed to have made quantitative estimations of the hydrogen peroxide produced. Tanaka (Biochem. Z. 1925, 157, 425) identified  $H_2O_2$  as a primary product of respiration when *Chlorella* was illuminated. It is generally held that hydrogen peroxide is an intermediate product in biological oxidations, although usually so rapidly decomposed that detectable concentrations are not formed. According to Avery and Morgan (J. Exp. Med. 1924, 39, 275) appreciable amounts accumulate in a broth culture of *Pneumococci* or of *Staphylococci* provided air is present and catalase, peroxydase and other enzymes which decompose  $H_2O_2$  are absent. Fromageot and Roux (Biochem. Z. 1933, 267, 202) found that the fermentation of sugar by *B. vulgaricus* is inhibited because of the accumulation of  $H_2O_2$ .

Hydrogen peroxide has also been found in the fermentation of tea (Biochem. J. 1939, 33, 836) in leaves of sugar cane (So and Nisioeda, Rept. Govt. Sugar Expt. Sta. Tainan, Formosa, 1939,

No. 6, 52); and in cultures of various bacteria such as *Pneumococci* (Johnstone, J. Path. Bact. 1940, 51, 59) and hamolytic *Streptococci* (Hadley and Hadley, J. Bact. 1940, 39, 21; Proc. Soc. Exp. Biol. Med. 1940, 43, 102).

#### FORMATION.

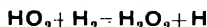
*From the Elements or Water.*—Small amounts of hydrogen peroxide have been detected in the water formed by the combustion of hydrogen in oxygen. Traube (Ber. 1885, 18, 1890, 1894) and Engler (*ibid.* 1900, 33, 1109) concluded that  $\text{H}_2\text{O}_2$  is the primary product of combustion: normally, it is decomposed at the high temperature, but appreciable quantities can be observed if the flame is cooled. Lewis and Randall, "Thermodynamics," 1923, however, calculated the theoretical amount of  $\text{H}_2\text{O}_2$  in the oxygen-hydrogen flame at 2,000–3,000°K. from the thermodynamics of the reaction:



and found that the concentration must be infinitesimal at that temperature, and, hence, the considerable amounts detected by Traube must be formed in the cooler parts of the flame, probably at 500–1,000°C.

Hydrogen peroxide is also formed in the explosion of hydrogen with excess oxygen; in a spark discharge under water; in a silent electric discharge through a mixture of water vapour and oxygen; in a Tesla discharge in moist air and in other similar circumstances. Fischer and Wolf (Ber. 1911, 44, 2956) succeeded in preparing a solution of hydrogen peroxide containing 86.9%  $\text{H}_2\text{O}_2$  by passing a silent electric discharge through a non-explosive mixture of oxygen and hydrogen (97%  $\text{H}_2$ , 3%  $\text{O}_2$ ) at the temperature of liquid air.

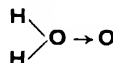
In all these modes of formation, the  $\text{H}_2\text{O}_2$  is probably derived from short-lived atoms, ions or free radicals (e.g.  $\text{OH}$  and  $\text{HO}_2$ ) by such reactions as:



(For the theory of combustion of hydrogen, see Hunselwood and Williamson, "The Reaction between Oxygen and Hydrogen," Oxford University Press, 1934.) Atomic hydrogen has been used to study the mechanism of formation of hydrogen peroxide (Taylor and Marshall, J. Physical Chem. 1925, 29, 842; Bonhoeffer and Loeb, Z. physikal. Chem. 1926, 119, 385, 474). More recently, Rodebush and his collaborators (J. Chem. Physics, 1933, 1, 696; *ibid.* 1936, 4, 293; J. Amer. Chem. Soc. 1937, 59, 1924) and others have investigated its production in an electrodeless discharge in water vapour.

Hydrogen peroxide is formed in the electrolysis of certain dilute aqueous solutions, but in most cases (e.g. with dilute sulphuric acid) this is not strictly formation from the elements but is rather a secondary product from the decomposition of per-compounds (see below). However, dissolved oxygen is reduced to  $\text{H}_2\text{O}_2$  by nascent electrolytic hydrogen at a mercury cathode (Foerster, "Elektrochemie wässriger Lösungen," 1922, p. 608). A glassy solid

formed by the action of atomic hydrogen on oxygen at  $-115^\circ$  may be the isomer



(Geib and Harteck, Ber. 1932, 65 [B], 1551).

Detectable amounts of  $\text{H}_2\text{O}_2$  are formed by irradiating pure water containing dissolved oxygen with X-rays or  $\alpha$ -,  $\beta$ - or  $\gamma$ -rays (Fricke, J. Chem. Physics, 1934, 2, 349, 556; Nurnberger, *ibid.* 1936, 4, 697). Ultra-violet light acts similarly in the presence of zinc oxide, which behaves as a photosensitiser (Baur and Neuweiler, Helv. Chim. Acta, 1927, 10, 901); otherwise very short ultra-violet is needed to produce any photochemical reaction. Sonic vibrations of frequency 9,000 (Flosdorf, Chambers and Malisoff, J. Amer. Chem. Soc. 1936, 58, 1069) and ultrasonic waves of frequency 540,000 Hz. (Schultes and Gohr, Angew. Chem. 1936, 49, 420) are said to produce traces of  $\text{H}_2\text{O}_2$  in water saturated with  $\text{O}_2$ .

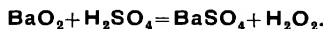
*In Oxidation Reactions.*—According to Lenher (J. Amer. Chem. Soc. 1931, 53, 2420, 3737, 3752) hydrogen peroxide is a secondary product of the combustion of hydrocarbons, and it has also been found in the condensate from flames impinging on ice of hydrogen, alcohol, coal gas, ether and carbon disulphide (Engler, Ber. 1900, 33, 1109) and methane (Riesenfeld and Gurian, Z. physikal. Chem. 1928, 139, 169).

Hydrogen peroxide is formed in certain so-called "autoxidation" reactions, including the slow oxidation of various organic materials such as turpentine in the presence of air and water (Kingzett, Chem. News. 1878, 38, 224), and when finely divided Zn, Mg or Al is shaken with water containing oxygen, or with dilute acids in the presence of air (Traube, Ber. 1893, 26, 1471; Fryling and Tooley, J. Amer. Chem. Soc. 1936, 58, 826; Müller and Barchmann, Z. Elektrochem. 1934, 40, 188). Furman and Murray (J. Amer. Chem. Soc. 1936, 58, 429) suggested that the formation of  $\text{H}_2\text{O}_2$  when mercury dissolves in dilute HCl saturated with oxygen probably occurs by way of  $\text{HO}_2$  produced from atomic hydrogen and molecular oxygen at the mercury surface. Similar views were expressed by Churchill (Trans. Electrochem. Soc. 1939, 76, 341) with regard to the corrosion of Al.

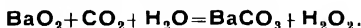
Certain autoxidation reactions in which hydrogen peroxide is formed have been proposed for its technical preparation. These include the oxidation of anthraquinone and similar substances by air or oxygen to quinonoid compounds, and of hydrazo- to azo-compounds (e.g. B.P. 489978–9). The formation of hydrogen peroxide in the enzymic oxidation of amino-acids *in vitro* (Bernheim *et al.*, J. Biol. Chem. 1936, 114, 657) and in other biological processes may be analogous. It is also said to be formed in catalytic dehydrogenations of MeOH and EtOH (Macrae, Biochem. J. 1933, 27, 1248).

*From Peroxides.*—Hydrogen peroxide is produced in good yield when metallic peroxides of the types  $\text{M}_2\text{O}_2$ ,  $\text{M}'\text{O}_2$ , are dissolved in dilute acids in the cold. The peroxides used are those of Ba, Na or K; the acids recommended include

$\text{H}_2\text{SO}_4$ ,  $\text{HF}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SiF}_6$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ , tartaric and carbonic, and the method is convenient if the salt formed is sparingly soluble. The most common method of preparation in the laboratory is by the addition of barium peroxide to the calculated quantity of cold (ca.  $10^\circ\text{C}$ .) dilute  $\text{H}_2\text{SO}_4$  (1 vol. acid to 5 vol. water):

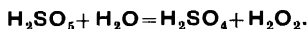


The filtrate, after removal of the precipitated barium sulphate, is a practically pure solution of  $\text{H}_2\text{O}_2$  of about "8-volume" strength (8 vol. of oxygen liberated from 1 vol. of solution by boiling with a catalyst). Carbon dioxide can be used instead of sulphuric acid:

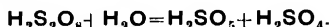


Combinations of other peroxides and other acids have been recommended (e.g.  $\text{K}_2\text{O}_2$  with tartaric acid), and the usual methods may be applied to precipitate excess salts or, alternatively, the hydrogen peroxide can be separated by distillation under reduced pressure.

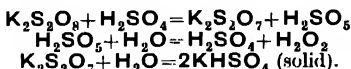
*From Per-Acids and Their Salts.*—Hydrogen peroxide is obtained very efficiently by the hydrolysis of permonosulphuric acid (Caro's acid):



In technical practice persulphuric acid (prepared by electrolysis) is distilled under reduced pressure, Caro's acid being formed as intermediate:

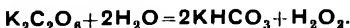


The hydrogen peroxide formed distils off and is obtained as a pure solution. Persulphates give hydrogen peroxide when warmed with acids:



Concentrated  $\text{H}_2\text{O}_2$  can therefore be produced by direct distillation from potassium or ammonium persulphate, provided a small amount of  $\text{H}_2\text{SO}_4$  is present.

Percarbonates similarly give  $\text{H}_2\text{O}_2$  by hydrolysis, even in the cold:



Perphosphates (e.g. potassium perdisphosphate,  $\text{K}_4\text{P}_2\text{O}_8$ ) and numerous other per-compounds may give rise to  $\text{H}_2\text{O}_2$ , although in practice many of them are prepared from it.

See also B.P. 297880, 316919; G.P. 528461, 333111; Lowenstein, Z. Elektrochem. 1928, 34, 784; Walton and Filson, J. Amer. Chem. Soc. 1932, 54, 3228.

#### TECHNICAL PREPARATION.

*The Persulphate Process.*—The electrolytic preparation of persulphates (see above), followed by their hydrolysis, has now become the chief method in use for the technical manufacture of hydrogen peroxide. (For a comprehensive account and list of patents, see Machu, "Das Wasserstoffperoxyd und die Perverbindungen,"

J. Springer, Vienna, 1937). The process has developed in three stages:

(1) Originally, persulphuric acid was made by the electrolysis of sulphuric acid, and hydrogen peroxide was separated by warming and vacuum distillation of the solution.

(2) Later, in place of sulphuric acid, ammonium sulphate dissolved in sulphuric acid was used as electrolyte, and the resulting ammonium persulphate was converted to the sparingly soluble potassium salt by adding  $\text{KHSO}_4$ . The potassium persulphate which separated was subjected to vacuum distillation with sulphuric acid and steam.

(3) More recently, ammonium persulphate solution has been vacuum-distilled directly without conversion to the potassium salt.

All three are cyclic processes as the residue from distillation is used again.

For a discussion of the theoretical principles which determine the efficiency obtained in the electrolytic preparation of persulphuric acid and persulphates, see Machu, *op. cit.*, Ch. X1; Essm *et al.*, Z. Elektrochem. 1927, 33, 107; 1933, 39, 891; 1935, 41, 261; Z. physikal. Chem. 1932, 162, 44; Riesefeld and Solowjan, *ibid.* 1931, Bodenstein-Festband, 405.

The following general conditions have been found desirable in practice. The anolyte must be very pure owing to the catalytic action of impurities such as heavy metal ions; it is necessary to repurify it at intervals by distilling the sulphuric acid in quartz vessels or by recrystallising the sulphate. For the same reason, all parts of the cell must be free from injurious impurities. For instance, the copper conductors must be lead-coated, or alternatively, lead or aluminium connections can be used. Smooth platinum is the best material for the anode, and since only a small surface area is required this may take the form of a thin strip of platinum foil on the surface of conducting bars of tantalum (G.P. 386514) or on aluminium (G.P. 591263) which has been previously anodically oxidised.

Various methods have been devised to avoid the use of a diaphragm to separate the anode and cathode compartments (e.g. G.P. 195811, 257276, 271642), but more often a thin diaphragm of unglazed porcelain, kieselguhr or synthetic resin is used, and in this case the cathode can be of lead. It is usually in the form of a coiled pipe through which cooling water is passed.

In general, the efficiency of persulphate formation increases with the anodic current density. With sulphuric acid as anolyte there is an optimum acid concentration (sp.gr. 1.60-1.45, depending on the current density). Replacement of some of the  $\text{H}_2\text{SO}_4$  by ammonium sulphate increases the efficiency considerably and, in fact, a recent process uses ammonium bisulphate alone. The volume of anolyte between the anode and diaphragm should be small; one arrangement (G.P. 567542) employs a thin film of liquid flowing rapidly over the electrode at a temperature of  $10-15^\circ\text{C}$ .

An example of a persulphate unit cell is shown in figs. 1 and 2, taken from G.P. 567542.

The anolyte flows into the cell through a glass tube (6) and then upwards through a narrow

space between the cylindrical porous pot (3) and a close-fitting glass vessel (5) and finally leaves the cell at the over-flow (4). Between (3) and (5) is the anode (12) which consists of a number of vertical Pt-Ta strips connected at the top (9). The cathode is a spiral lead pipe (14) through which cold water circulates, eventually passing into the inner vessel (5) and out at the top. When a number of cells are worked in series the catholyte and anolyte are fed into the first cell (which is highest) and then flow from cell to cell by gravity. With sulphuric acid as electrolyte an anodic current density of 0.6–0.8 amp. per sq. cm. is used. If the anode compartment is 5 cm. in diameter, 50 cm. high and 0.2–0.3 cm. thick the capacity is 180–230 c.c.

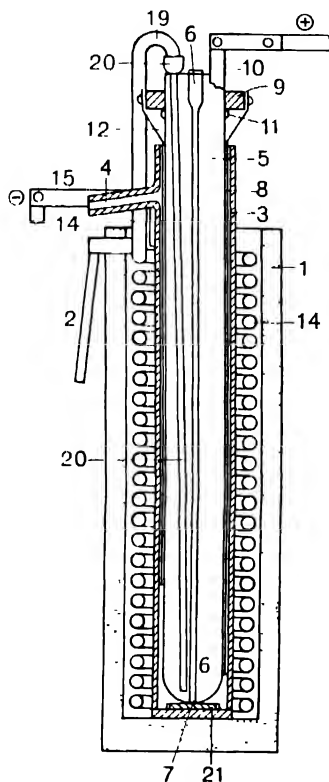


FIG. 1.—DIAGRAM OF THE WEISSENSTEINER PERSULPHATE CELL (Machu, *op. cit.*, Fig. 13).

The rate of flow of anolyte is about 3.25 c.c. per amp. per minute, and a current of 80–100 amp. is used. This requires 5–6 volts per cell. Under these conditions persulphuric acid of concentration 25–30% is produced from  $\text{H}_2\text{SO}_4$  of sp.gr. 1.285 with a current efficiency of more than 70%. Using ammonium bisulphate as electrolyte an efficiency of 85% can be obtained.

Hydrogen peroxide is prepared from the persulphate solution by hydrolysis and vacuum distillation. In one method (Fig. 3) (F.P. 733201) the solution is heated to 50–60°C. and then atomised into an evacuated, heated column (in

some cases with the addition of steam). The acid mist passes into a separator whence the water and  $\text{H}_2\text{O}_2$  vapour are removed and condensed while the residual liquid (e.g. ammonium bisulphate) runs back *via* a cooler and pump to the electrolytic cell. The distillation can be carried out with an efficiency of about 95%. The flow diagram of a typical continuous flow process is shown in fig. 3.

The energy required to produce 1 kg. of 30% hydrogen peroxide by any of the three con-

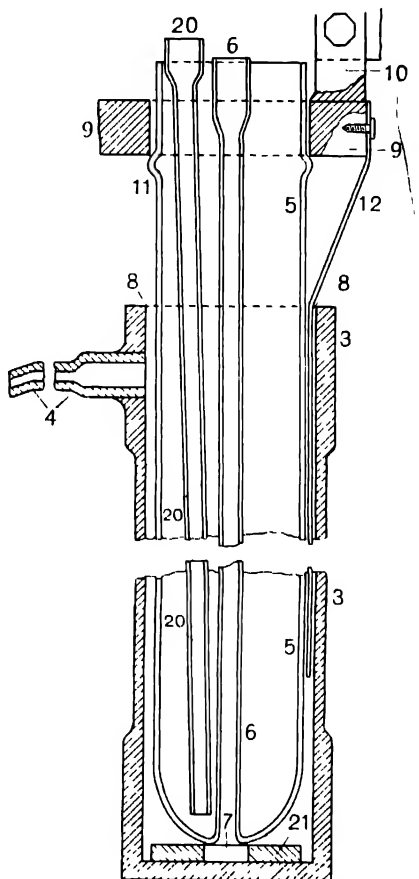


FIG. 2.—DETAILS OF THE ANODE COMPARTMENT (Machu, *op. cit.*, Fig. 15).

tinuous persulphate processes is about 4–5 kilowatt-hours.

**The Barium Peroxide Process.**—This method of preparing  $\text{H}_2\text{O}_2$ , although the oldest known, is still in use to some extent, largely owing to the fact that the fine white pigment 'blanc fixe' is obtained at the same time. The chief difficulties are that a very pure  $\text{BaO}_2$  must be used, and that the  $\text{H}_2\text{O}_2$  is obtained only as a dilute solution. The first difficulty necessitates a long method of preparation from barytes; the second is less serious now that efficient vacuum distillation is available. The usual method for the

preparation of pure  $\text{BaO}_2$  involves the following steps:

(1) Ground barytes mixed with coke is heated in a rotary kiln to give barium sulphide ( $\text{BaS}$ ).

(2) The kiln clinker ( $\text{BaS}$ ) is lixiviated with water, and barium carbonate is precipitated by the addition of soda ash.

(3) The barium carbonate is mixed with carbon and heated to  $1,200^\circ$  in a furnace to form barium monoxide ( $\text{BaO}$ ).

(4) This  $\text{BaO}$  when heated in a stream of purified air at  $540^\circ\text{C}$ . is oxidised to barium per-

oxide, which is the immediate starting-point in the chemical preparation of hydrogen peroxide.

The barium peroxide is decomposed in the cold with either dilute sulphuric or phosphoric acid; more concentrated  $\text{H}_2\text{O}_2$  can be made by use of the latter (15% as against 3-6% with  $\text{H}_2\text{SO}_4$ ) and the precipitated barium phosphate is easily filterable and carries down with it impurities like iron, manganese, etc., leaving a pure solution of  $\text{H}_2\text{O}_2$  of good stability. In technical practice the decomposition of  $\text{BaO}_2$  gives a 95% yield. (Phosphoric acid is recovered

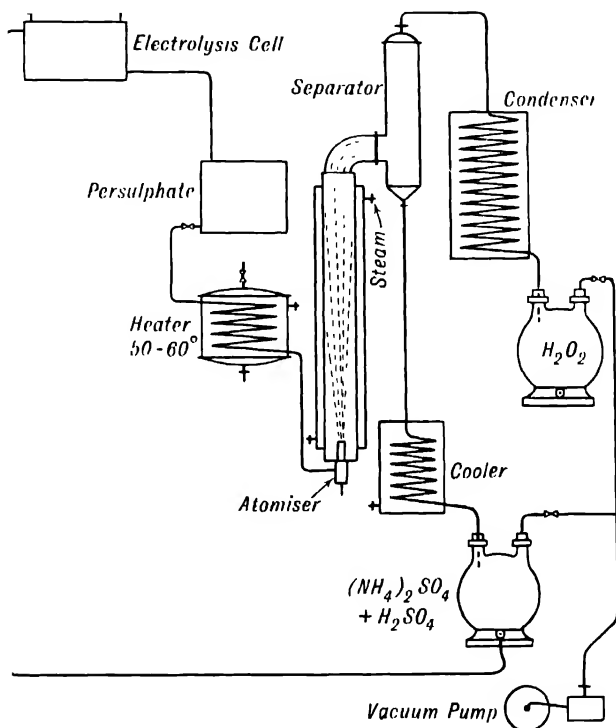


FIG. 3.—DIAGRAM OF PLANT FOR THE CONTINUOUS DISTILLATION OF HYDROGEN PEROXIDE FROM AMMONIUM PERSULPHATE SOLUTION (Machu, *op. cit.*, Fig. 35).

by adding  $\text{H}_2\text{SO}_4$  to the barium phosphate, and the precipitated  $\text{BaSO}_4$  is used as a pigment ("blanc fixe"). A convenient way of removing impurities from the regenerated phosphoric acid has been patented (G.P. 435900.)

The dilute  $\text{H}_2\text{O}_2$  obtained in the  $\text{BaO}_2$  process is commonly concentrated to 30-40% by distillation and rectification. Table I shows, for example, that the distillate from 14.2%  $\text{H}_2\text{O}_2$  boiling at  $30.8^\circ\text{C}/17$  mm. contains only 0.58%  $\text{H}_2\text{O}_2$ ; hence, the residue becomes more concentrated. (For examples of rectification plant, see F.P. 563908, G.P. 525923.)

#### PHYSICAL PROPERTIES.

Solid  $\text{H}_2\text{O}_2$  (Staedel, Z. angew. Chem. 1902, 15, 642), large prisms from 95%  $\text{H}_2\text{O}_2$  cooled

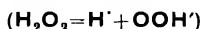
TABLE I.—(Machu, *op. cit.*, Table 14, p. 152.)  
17 mm. Hg.

Boiling point $^\circ\text{C}$ .	Concentration of residue in weight, %.	Concentration of distillate in weight, %.
21.0	5.5	0.21
23.0	5.7	0.22
25.5	6.85	0.23
26.6	8.0	0.34
28.5	9.8	0.45
30.8	14.2	0.58
33.3	19.2	1.05
35.5	24.5	1.3
38.2	32.0	2.9
40.5	48.8	10.4

with ether-carbon dioxide. M.p.  $-0.89^{\circ}\text{C}$ . (Cuthbertson *et al.*, J. Amer. Chem. Soc. 1928, 50, 1120).

Pure  $\text{H}_2\text{O}_2$  is a colourless liquid, the physical properties of which are very sensitive to the addition of traces of water. Published data are rather discordant, but the following list gives probable values. Much of the recent work is due to Maass and co-workers (*ibid.* 1920, 42, 2548, 2569; 1922, 44, 2472; 1924, 46, 2693; 1929, 51, 674; 1930, 52, 489).

Density (liq.)  $d_4^{20} = 1.4649$ ; b.p.  $151.4^{\circ}\text{C}/760$  mm.; latent heat of vaporisation 11,610 cal. per g.-mol.; Trouton's constant 27.3; surface tension at  $18.2^{\circ}\text{C}$ . 75.94 dynes/cm.; magnetic susceptibility (diamagnetic)  $8.8 \times 10^{-7}$  e.m.u.; specific conductivity  $2 \times 10^{-6}$  ohm $^{-1}$ ; specific conductivity of 4.5% solution  $2.89 \times 10^{-8}$  ohm $^{-1}$ ; dissociation constant



at  $25^{\circ}$   $2.4 \times 10^{-12}$ ; heat of ionisation  $8.6 \times 10^3$  cal. per g.-mol.; oxidation potential of  $\text{H}_2\text{O}_2$   $-1.81 \pm 0.03$  volts; reduction potential  $-0.66 \pm 0.03$  volt; dielectric constant of pure  $\text{H}_2\text{O}_2$  93.7, of 20.8%  $\text{H}_2\text{O}_2$  113.5; mean coefficient of expansion  $-10^{\circ}$  to  $+20^{\circ}$ , 0.00107; latent heat of fusion 74 cal. per g.; specific heat (liq.) 0.579, (solid) 0.470; viscosity at  $18^{\circ}$  0.0130 poises;  $\eta_{10}^{22} = 1.4139$ ; heat of formation ( $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2(\text{liq.})$ ) 45,320 cal. per g.-mol.; heat evolved in decomposition ( $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$ ) 23,450 cal. per g.-mol.; heat of solution in water 460 cal.; vapour pressure is given by the equation.

$$\log_{10} p_{\text{mm.}} = 8.853 - \frac{(0.05223 \times 48530)}{T}$$

Dipole moment 2.1 D.; mol. wt. (from v.d.) 34; partition coefficient of  $\text{H}_2\text{O}_2$  between water and ether 0.043.

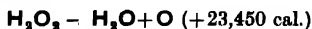
Hydrogen peroxide is miscible with water in all proportions; Table II gives the relation between the density at  $18^{\circ}$ , the composition by weight (g.  $\text{H}_2\text{O}_2$  in 100 g. solution), the composition by volume per cent. and the number of volumes of oxygen gas evolved when the solution is decomposed.

Hydrogen peroxide is soluble in alcohol, ether and quinoline, but not in dry benzene or petroleum spirit.

The infra-red absorption spectrum of liquid and gaseous  $\text{H}_2\text{O}_2$  has been studied by Baly and Gordon (Trans. Faraday Soc. 1938, 34, 1133).

#### CHEMICAL PROPERTIES.

The structure of hydrogen peroxide is  $\text{H}-\text{O}-\text{O}-\text{H}$ . The majority of its reactions depend on the ease with which one oxygen atom is given off:



This leads to both oxidising and reducing properties. In addition,  $\text{H}_2\text{O}_2$  acts as an extremely weak acid and gives rise to many per-compounds containing the  $-\text{O}-\text{O}-$  bridge. Finally, it forms numerous addition compounds.

*Oxidation.*—Hydrogen peroxide is a powerful

TABLE II.—(Machu, *op. cit.*, Table 7, p. 37.)

Density, $d_4^{18}$	Weight, %.	Volume, %.	Volumes of oxygen.
0.9986	0	0	0
1.0018	1.0	1.0	3.3
1.0034	1.5	1.5	5
1.0050	2.0	2.0	6.6
1.0083	3.0	3.0	10
1.0134	4.55	4.55	15
1.0151	5.0	5.1	17
1.0187	6.0	6.15	20
1.0241	7.5	7.7	25
1.0336	10.0	10.35	34
1.0526	15.0	15.8	52
1.0717	20.0	21.45	70
1.0911	25.0	27.3	90
1.1023	27.2	30.0	100
1.1111	30.0	33.33	110
1.1331	35.0	39.7	132
1.1561	40.0	46.25	153
1.1796	45.0	53.1	175
1.2031	50.0	63.15	208
1.2505	60.0	75.05	248
1.2980	70.0	90.85	300
1.3456	80.0	107.65	355
1.3936	90.0	125.4	415
1.4442	100.0	144.4	475

oxidising agent. It reacts with sulphites, sulphides, thiosulphates, tetrathionates, etc., to give sulphates. Nitrous acid is oxidised to nitric as is also hydroxylamine sulphate at  $60^{\circ}$ . Aqueous ammonia gives ammonium nitrite and nitrate, but at  $-48^{\circ}$  in ether the crystalline compound  $(\text{NH}_4)_2\text{O}_2 \cdot \text{H}_2\text{O}$  is deposited. Stannous salts give stannic, ferrous give ferric, etc. Concentrated  $\text{H}_2\text{O}_2$  oxidises As, Se and Te to arsenic, selenic and telluric acids, while yellow phosphorus reacts at  $60^{\circ}$  to form phosphine and phosphorous and phosphoric acids.

Hydrogen peroxide reacts with  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{HI}$ , but it is stabilised by  $\text{HF}$  (Maass and Hiebert, J. Amer. Chem. Soc. 1924, 46, 290). The reaction with  $\text{HCl}$  is slow, the products being  $\text{HOCl}$ ,  $\text{Cl}_2$  and oxygen;  $\text{HBr}$  reacts much more rapidly.

Al and Mg dissolve slowly in concentrated  $\text{H}_2\text{O}_2$  forming hydroxides. Sodium amalgam reacts more strongly with  $\text{H}_2\text{O}_2$  than with water. Cu, Ag, Hg, Ni and Bi dissolve in dilute  $\text{H}_2\text{SO}_4$  in the presence of  $\text{H}_2\text{O}_2$ , but Sn, Pb, Au, Pt and Sb do not. The decomposition of  $\text{H}_2\text{O}_2$  by Hg is a periodic phenomenon (Okaya, Proc. Phys.-Math. Soc. Japan, 1919, 1, 283).

A large number of organic substances are oxidised by  $\text{H}_2\text{O}_2$ , the extent of oxidation depending on conditions such as concentration and the presence of promoters (*see below*). Polyalcohols give aldehydes; oxalic acid is broken down into  $\text{CO}_2$  and water; tartaric acid gives dihydroxymaleic acid; sugars form ozonides; benzene is oxidised to phenol. In alkaline solution  $\text{H}_2\text{O}_2$  oxidises  $\text{R} \cdot \text{CS} \cdot \text{NHR}'$  to  $\text{R} \cdot \text{CO} \cdot \text{NHR}'$ . Alkaloids give new crystalline bases which are often highly coloured. Indigo

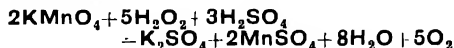
is slowly decolorised. An unusual reaction occurs between  $\text{H}_2\text{O}_2$  and formaldehyde in alkaline solution, hydrogen gas being evolved:



The oxidation of organic materials by  $\text{H}_2\text{O}_2$  is catalysed by some substances which themselves accelerate its decomposition. For instance, in the presence of ferric salts  $\text{H}_2\text{O}_2$  oxidises alcohol to acetic acid. Walton and Graham (J. Amer. Chem. Soc. 1928, 50, 1641) studied the catalysed oxidation by  $\text{H}_2\text{O}_2$  of organic acids such as succinic, lactic, etc., and also of ethylene glycol and glycerol to  $\text{CO}_2$  and water with ferric chloride,  $\text{CuO}$  and  $\text{CuSO}_4$  as catalysts. The addition of  $\text{H}_2\text{O}_2$  to  $\alpha\beta$ -unsaturated ketones (in ether or benzene) to give the dihydroxyketones is catalysed by  $\text{OsO}_4$  (Butenandt and Wolz, Ber. 1938, 71 [B], 1483). The oxidation of dienes by  $\text{H}_2\text{O}_2$  is catalysed by ferric hydroxide.

Organic materials such as paper inflame when treated with highly concentrated  $\text{H}_2\text{O}_2$ .

**Reduction.**—Besides producing oxidation, the nascent oxygen atom from  $\text{H}_2\text{O}_2$  can attach itself to a similar oxygen atom of other oxidising agents, and thus apparently cause reduction with the evolution of oxygen gas. For example, potassium permanganate is reduced to  $\text{MnO}_2$  in alkaline solution or to  $\text{MnSO}_4$  in the presence of  $\text{H}_2\text{SO}_4$ :



Ferricyanides are reduced to ferrocyanides in alkaline solution, but in acid or neutral solution the reverse reaction occurs. Silver oxide is reduced to metallic silver;  $\text{NaOI}$  gives  $\text{NaI}$ ;  $\text{Ca}(\text{OCl})_2$  gives  $\text{CaCl}_2$ .

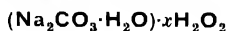
**Formation of Per-Compounds.**—The true per-compounds contain the  $-\text{O}-\text{O}-$  bridge; a large number are known to exist, but many are unstable. Many per-compounds are formed directly from  $\text{H}_2\text{O}_2$  which can be regarded as a very weak acid. The addition of  $\text{H}_2\text{O}_2$  to an aqueous solution of  $\text{NaOH}$  gives sodium peroxide,  $\text{Na}_2\text{O}_2$ . Unstable peroxides of  $\text{Zn}$ ,  $\text{Mg}$ ,  $\text{Cd}$  are formed by the action of  $\text{H}_2\text{O}_2$  on the metal hydroxides; those of  $\text{Zr}$ ,  $\text{Ce}$ ,  $\text{Th}$ ,  $\text{Y}$ ,  $\text{La}$ ,  $\text{Sm}$  are obtained from the oxides. The addition of ammonia to a solution of  $\text{CaCl}_2$  and  $\text{H}_2\text{O}_2$  precipitates  $\text{CaO}_2$ .

Sulphuric acid reacts with  $\text{H}_2\text{O}_2$  to give Caro's acid, permonosulphuric acid,  $\text{HO}\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$ ; similarly acetic acid yields peracetic acid. Permonophosphoric acid is not formed in this way from orthophosphoric acid, but can be made by the reaction:  $2\text{H}_2\text{O}_2 + \text{P}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{H}_3\text{PO}_6$ . The true percarbonates ( $\text{K}_2\text{C}_2\text{O}_6$ ,  $\text{Na}_2\text{CO}_4$ ) are not obtainable directly from  $\text{H}_2\text{O}_2$ , only the carbonate perhydrates being formed (v.i.). Many per-compounds are strongly coloured; for example, the addition of  $\text{H}_2\text{O}_2$  to solutions of  $\text{TiO}_2$  gives the intense yellow of pertitanic acid (hydrated  $\text{TiO}_2$ ). Perchromates are formed by adding  $\text{H}_2\text{O}_2$  to soluble chromates (v. Vol. III, 114a). Salts of  $\text{Mo}$ ,  $\text{Ce}$ ,  $\text{Va}$ ,  $\text{Nb}$ ,  $\text{U}$  and  $\text{W}$  also give coloured (mostly yellow) solutions of unstable per-compounds. For example,

uranyl nitrate and  $\text{H}_2\text{O}_2$  form  $\text{UO}_4\cdot 2\text{H}_2\text{O}_2$ . Pertantalates are white powders (see Emcléus and Anderson, "Modern Aspects of Inorganic Chemistry," G. Routledge, London, 1938, p. 356).

**Addition Reactions.**—A number of stable compounds can be prepared from  $\text{H}_2\text{O}_2$  by simple addition.  $\text{H}_2\text{O}_2$  combines with ammonium sulphate, sodium sulphate, borate, phosphate, acetate and arsenate as "hydrogen peroxide of crystallisation." It forms crystalline compounds such as  $\text{Na}_2\text{O}_2\cdot 2\text{H}_2\text{O}_2$  with the alkali and alkaline earth peroxides.

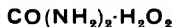
The "sodium perborate" ("Perborax," "Perorydol") of industry is  $\text{NaBO}_2\cdot \text{H}_2\text{O}_2\cdot 3\text{H}_2\text{O}$  and can be made by mixing sodium borate solution with hydrogen peroxide in the cold (v. Vol. II, 51d-52b). When dry, it is completely stable, while its solutions possess oxidising powers like  $\text{H}_2\text{O}_2$ . It is used extensively in washing powders and for bleaching. A large number of sodium carbonate perhydrates such as  $2\text{Na}_2\text{CO}_3\cdot 3\text{H}_2\text{O}_2$  and a series



where  $x = \frac{1}{2}, 1, 1\frac{1}{2}, 2, 2\frac{1}{2}$  are known. They can be prepared by adding anhydrous sodium carbonate to a suitable amount of  $\text{H}_2\text{O}_2$  solution. The carbonate perhydrates are more stable (and therefore of greater technical importance) than the true percarbonates. Many phosphate perhydrates and silicate perhydrates can be obtained similarly.

Hydrogen peroxide forms addition compounds with acetamide, urethane, succinimide, asparagine, pinacol, strychnine, erythrose and mannose. Addition compounds of  $\text{H}_2\text{O}_2$  with ammonia, ethylamine, propylamine, butylamine and pyridine have been obtained from ethereal solution.

Of special interest is the compound



("Hyperol," "Perhytrite," "Ortizon") which is prepared by cooling a solution of urea dissolved in 30%  $\text{H}_2\text{O}_2$  to  $-5^\circ$ . It is a stable white powder, soluble in  $2\frac{1}{2}$  parts of water. It provides a convenient form of "solid"  $\text{H}_2\text{O}_2$  for pharmaceutical and analytical purposes (Boover, Chem. and Ind. 1925, 44, 1137).

#### DECOMPOSITION.

Hydrogen peroxide is thermochemically unstable; its decomposition into water and oxygen is exothermic to the extent of 23,450 cal. per g.-mol. However, pure  $\text{H}_2\text{O}_2$  and its pure solutions keep well at ordinary temperatures and decompose only comparatively slowly when heated, with the exception that the pure liquid explodes at about  $151^\circ\text{C}$ . Apparently the true homogeneous decomposition of liquid or vapour requires a high energy of activation, and even the slow reaction of  $\text{H}_2\text{O}_2$  vapour in a quartz flask at  $85^\circ$  occurs heterogeneously on the walls, but the decomposition is greatly accelerated by the catalytic action of solid surfaces (particularly carbon, platinum and manganese dioxide); by heavy metal ions (notably  $\text{Fe}$  and  $\text{Cu}$ , but also salts and oxides of  $\text{Pb}$ ,  $\text{Hg}$ ,  $\text{Co}$ ,  $\text{Ni}$  and  $\text{Mn}$ , etc.);

by natural enzymes; or by irradiation with ultra-violet light or X-rays.

Very concentrated  $\text{H}_2\text{O}_2$  explodes when brought into contact with an effective catalyst such as  $\text{MnO}_2$ .

Catalysis at the surfaces of dispersed solids has been the subject of many investigations. The most effective material known is an osmium sol which still exerts a strong catalytic action at dilutions as great as 10<sup>-6</sup> g. per c.c. Other metals in colloidal form (particularly Pd, Pt, Ir, Au and Ag) are also very effective, as are  $\text{MnO}_2$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{PbO}_2$  and copper peroxide. High surface area naturally enhances the effect of a solid (sugar charcoal, for instance, is very active), but the nature of the solid is particularly important. According to Wright and Kideál (Trans. Faraday Soc. 1928, 24, 530) the velocity of catalytic decomposition of  $\text{H}_2\text{O}_2$  by sugar charcoal, iron oxide,  $\text{Mg}(\text{OH})_2$ , kaolin,  $\text{WO}_3$ , glass,  $\text{CrCl}_3$ , ZnO and silica gel is very dependent on traces of acids, alkalis or heavy metals, and it reaches a maximum at a  $\text{pH}$  corresponding to the isoelectric point of the surface. On the other hand, hæmin and the chemically related iron compounds of the porphyrin group exert an enormous and virtually specific catalytic effect on the decomposition of  $\text{H}_2\text{O}_2$ . Natural enzymes possessing the specific property of destroying hydrogen peroxide occur widely in animal and vegetable tissues and are known collectively as "catalases" (*q.v.*).

The metal-sol catalysts (Pt, Ag, etc.) are very susceptible to "poisoning" by minute quantities of sulphides, arsine, HCN, CO,  $\text{HgCl}_2$ , phosphine, phosphorus,  $\text{CS}_2$ , phenol, strychnine, iodine, etc., whereby their catalytic activity is largely reduced or destroyed (*see*, for example, Bredig and Ikeda, Z. physikal. Chem. 1901, 37, 1). The effectiveness of positive catalysts is also impaired to a greater or less extent by many capillary-active substances which are probably preferentially adsorbed on the surface of the solid; among these are alcohols, ketones, uric acid, barbituric acid, etc.

**Stabilisers.**—Solution of  $\text{H}_2\text{O}_2$  are slowly decomposed by alkalis (as, for example, from soda-glass bottles), and hence their stability is improved by acids (*e.g.* 0.1% of  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ ). In addition, a very large number of substances have been proposed as general stabilisers; phenacetin and salicylic acid (0.1–0.5 g. per litre) are suitable for pure  $\text{H}_2\text{O}_2$  solutions; other substances claimed include: pyro- and meta-phosphates of Na, Mg, Ca, Sn, magnesium and sodium silicates, sodium benzoate, acetanilide, methyl *p*-hydroxybenzoate ("nipagin"), hexamine, tannin, naphthylamine, numerous alcohols, ketones, aldehydes, amides, ether, glycerol, pyrogallol, oxalic acid and many other diverse organic compounds. Sodium and calcium chlorides are appreciably preservative if used in large amount. Modern pure preparations of  $\text{H}_2\text{O}_2$  scarcely need stabilising, but in technical use, as in bleaching baths, destructive impurities may be introduced, and a suitable stabiliser may reduce loss of peroxide.

**Storage.**—Stabilised  $\text{H}_2\text{O}_2$  solutions can be stored in glass, porcelain or stoneware vessels,

while small quantities of pure 30%  $\text{H}_2\text{O}_2$  are commonly kept in paraffin wax bottles. There is some fire danger in the transport of 30%  $\text{H}_2\text{O}_2$  owing to its powerful oxidising action on organic materials, but it has been found possible to store large quantities in tanks of treated aluminium or of certain aluminium and other alloys, provided suitable stabilisers are added. The addition of ammonium nitrate or nitric acid to  $\text{H}_2\text{O}_2$  is aluminium.

#### TECHNICAL APPLICATIONS.

Hydrogen peroxide is extensively used as a bleaching agent, antiseptic and preservative on account of its powerful oxidising properties.

**Bleaching** is carried out with warm, mildly alkaline solutions containing suitable stabilising agents such as water-glass. Injurious impurities (*e.g.* traces of Fe and Cu) must be carefully excluded from the bleaching bath to avoid waste of  $\text{H}_2\text{O}_2$ , and when not in use the bath may be acidified to improve its stability. For mild bleaching a concentration of about 0.2%  $\text{H}_2\text{O}_2$  is used at 40–45°C., while more powerful action can be obtained by using stronger solutions and higher temperatures (*e.g.* 3%  $\text{H}_2\text{O}_2$  at 80°C.). Hydrogen peroxide can be used to bleach practically any material; among those mentioned in the literature are all forms of cotton, wool, silk, linen (*v. Vol.* 11, 10c, 17a, 18c), furs, skins, wood, horse hair, parchment, feathers, hoof, horn, bones, ivory, fats and oils. For many purposes  $\text{H}_2\text{O}_2$  may be replaced by its stable solid derivatives, the carbonate and borate perhydrates. Sodium perborate may be incorporated in soaps and is extensively used in laundering.

**As a Disinfectant and Preservative.**—Bacteria are rapidly destroyed by dilute solutions of  $\text{H}_2\text{O}_2$ : *Staphylococci* and diphtheria bacilli are killed by 1.75%  $\text{H}_2\text{O}_2$  within 5 minutes (*v. Vol.* IV, 19a). A 3%  $\text{H}_2\text{O}_2$  solution has an antiseptic power equivalent to 1 in 1,000  $\text{HgCl}_2$  and has the advantage of being non-poisonous (although concentrated  $\text{H}_2\text{O}_2$  blisters the skin). Dilute  $\text{H}_2\text{O}_2$  was formerly used as a preservative for milk, meat, gelatin, glue and cocoa-milk beverages but its use in food is not now permitted (*v. FOOD PRESERVATIVES*); fish has been packed in ice containing  $\text{H}_2\text{O}_2$ . Cut flowers are said to last much longer in very dilute  $\text{H}_2\text{O}_2$ . It has also been suggested for disinfecting seeds and as a leavening agent in place of yeast.

For pharmaceutical purposes the "10-volume" and "20-volume" solutions with sodium pyrophosphate or urea as stabiliser are generally used, and are further diluted a number of times. The very dilute solution is useful for cleaning or sterilising new or septic wounds and to stop bleeding; as an eye lotion, gargle or mouth wash; for external application in skin diseases; for burns and scalds, and to whiten the teeth. The solutions have a somewhat metallic taste.

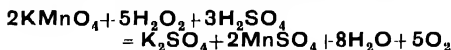
#### DETECTION AND ESTIMATION.

**Qualitative Identification.**—The following are probably the most sensitive and characteristic of the numerous tests which are available for



hydrogen peroxide. (1) The orange-coloured pertitanic acid is formed when  $\text{H}_2\text{O}_2$  is added to a solution of  $\text{TiO}_2$  in sulphuric acid (detects 1 part  $\text{H}_2\text{O}_2$  in  $1.8 \times 10^6$  parts of water). (2) A solution of  $\text{H}_2\text{O}_2$  is treated with 1 drop of dilute  $\text{H}_2\text{SO}_4$ , 2 c.c. of ether, and 1 drop of 1% potassium dichromate, and shaken, the characteristic blue colour of perchromic acid is formed in the ether layer (limit 0.2 mg. in 20 c.c.). (3) The guaiacum test is the most sensitive for  $\text{H}_2\text{O}_2$ . The solution to be tested is mixed with a fresh 1–2% solution of guaiacum resin in 90–98% alcohol until a slight turbidity develops; then one drop of an extract of malt is added, a blue colour is produced which serves to detect 1 part of  $\text{H}_2\text{O}_2$  in  $5 \times 10^7$  parts of water. (4) The solution containing  $\text{H}_2\text{O}_2$  is added to a reagent containing tartaric acid, potassium iodide and ferrous sulphate; after mixing, 5 or 6 drops of  $\text{NaOH}$  solution are added, a violet colour is formed (detects 1 in  $25 \times 10^6$ ). (5) Several sensitive spot tests are available, such as the bleaching of lead sulphide paper, the formation of Prussian Blue from a solution containing ferric chloride and potassium ferricyanide, or the formation of a red or blue gold colloid by reduction of gold salts. (*See also* Vol. II, 574a.)

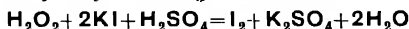
**Quantitative Determination.**—(1) By titration with potassium permanganate solution in the presence of a large excess of sulphuric acid.



1 c.c. of  $N/10$   $\text{KMnO}_4 = 0.001701$  g. of  $\text{H}_2\text{O}_2$ .

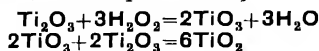
This method cannot be used if organic preservatives are present.

(2) The reaction with  $N/10$  iodine and alkali subsequently acidified gives in effect:



the liberated iodine being titrated with sodium thiosulphate using starch at the end-point in the usual way.

(3) With titanous chloride. On treating  $\text{H}_2\text{O}_2$  with a dilute solution of  $\text{Ti}_2\text{O}_3$  in the presence of acid the deep orange colour of pertitanic acid develops. This may be used to estimate  $\text{H}_2\text{O}_2$  directly by colorimetry, or alternatively, further  $\text{Ti}_2\text{O}_3$  may be added until the colour is just bleached; the end-point is sharp.



The titanous chloride is standardised in an inert atmosphere with iron alum; when the  $\text{Fe}^{++}$  colour has practically disappeared a drop of potassium thiocyanate solution is added and the titration continued to complete decolorisation (Knecht and Hibbert, *Ber.* 1906, 38, 3324). This method of determining  $\text{H}_2\text{O}_2$  is particularly useful when organic substances are present.

(4) Another method of determining  $\text{H}_2\text{O}_2$  is by measurement of the volume of oxygen evolved when the solution is decomposed by catalysts, by hypobromite or by potassium permanganate.

(5) Other methods based on potassium iodate, ceric sulphate, sodium arsenite, or manganic sulphate are also applicable.

M. C. and J. A. K.

## HYDROGEN SWELLS (v. Vol. V, 291a).

**HYDROGENATION** has come to be regarded as the combination of organic substances with hydrogen under the influence of a catalyst; the present article is concerned with the laboratory aspects of the subject. Articles on hydrogenation reactions of special importance in industry will be found in the appropriate places in the Dictionary.

Historically the first example of a catalytic hydrogenation was the production of methylamine by passing a mixture of hydrogen and hydrogen cyanide over platinum black (Debus, *Annalen*, 1863, 128, 200). The development of this vapour-phase method of hydrogenation is due mainly to Sabatier and Senderens and their co-workers (1897–1914). Since 1905 development has been mainly along the lines of using finely divided metals in the liquid phase (Willstätter, Pual, Skita, Adams, Adkins). This method of liquid-phase hydrogenation has, for the most part, ousted the vapour-phase method in laboratory, and largely in industrial, practice.

## GENERAL.

### VAPOUR-PHASE HYDROGENATION.

The apparatus in its simplest form consists of a hard-glass combustion tube, packed with a suitable catalyst and heated in a furnace (preferably electric). Hydrogen is passed through the tube and the substance is most conveniently introduced by bubbling the hydrogen through the liquid material heated to a suitable temperature. Such an apparatus was used by Sabatier and Senderens in their classical series of investigations (for summaries, see *Ann. Chim. Phys.* 1905, [viii], 4, 319; Sabatier, transl. Reid, "Catalysis in Organic Chemistry," 1923). The following are two typical catalysts used in these experiments:

(1) Pumice, broken up into small pieces, is boiled with nitric acid, washed with water and then saturated with a concentrated solution of sufficient nickel nitrate to give a catalyst of the desired nickel content. The product is then evaporated to dryness with good stirring and finally heated in a nickel dish over a free flame until the nickel nitrate is completely decomposed. The product is packed into the hydrogenation tube and, after sweeping out with hydrogen, reduced by heating to 300–400° in a stream of hydrogen. After cooling in hydrogen the tube is ready for use.

(2) Sixty grams of kieselguhr, purified by boiling with nitric acid and with water, are made into a paste with an aqueous solution of nickel nitrate. An excess of sodium carbonate solution is added and the mixture is boiled for a few minutes. After washing several times with hot water by decantation, the precipitate is filtered off, dried and then reduced as described for the pumice catalyst.

Such catalysts may be used for the reduction of ethylenic linkages (at about 100–150°), aromatic nuclei (about 200°), carbonyl- and nitro-groups.

A somewhat analogous but much more convenient vertical apparatus has been devised by Lush (*J.S.C.I.* 1923, 42, 219T; cf. Pelly, *ibid.*

1927, 46, 449T). In this apparatus the catalyst consists of nickel turnings which, before use, are first coated with an oxide film by anodic oxidation and then reduced in hydrogen. The apparatus may be used under pressure and has found application on a semi-technical scale and in laboratory operations; it is marketed by Messrs. Technical Research Works, Ltd. The apparatus is particularly suitable for routine laboratory hydrogenations on a fairly large scale; it has the advantage of being simple to operate and requires no expensive catalyst.

#### LIQUID-PHASE HYDROGENATION.

**Apparatus.**—The simplest form of apparatus may easily be assembled from ordinary laboratory equipment; it consists of a calibrated hydrogen-reservoir connected to a hydrogenation flask which is mounted for mechanical shaking. An arrangement for evacuating the flask is necessary and it is an advantage to arrange also for heating. To carry out a hydrogenation the substance to be hydrogenated, dissolved or suspended in a suitable solvent, is introduced into the hydrogenation vessel together with the catalyst. After evacuation, hydrogen is admitted and the flask is shaken until the required amount of hydrogen has been taken up; the flask is then once more evacuated, air is admitted, the catalyst is filtered off and the product isolated in an appropriate manner. Many forms of apparatus of this type have been described in detail in the literature (Paal and Gerum, *Ber.* 1908, 41, 813; Willstätter and Hatt, *ibid.* 1912, 45, 1472; Skita and Meyer, *ibid.* 1912, 45, 3594; Stark, *ibid.* 1913, 46, 2335). A similar apparatus adapted for working at pressures up to 3.5 atm. has been described by Adams and Voorhees (*Organic Syntheses*, 1928, 8, 10) and compact modifications are marketed by several firms; the hydrogen reservoir is a stout metal tank and the hydrogen-uptake is followed by the fall in hydrogen pressure during the reaction. This type of apparatus is well suited for general laboratory use.

It is frequently necessary, or at any rate desirable, to carry out hydrogenations at comparatively high temperatures and pressures. Adkins (*J. Amer. Chem. Soc.* 1933, 55, 4272) has designed an apparatus suitable for hydrogenations at temperatures up to 400° and pressures up to 300 atm. It consists essentially of a specially designed autoclave mounted on a shaker and fitted with an electrical heater. A modification of this apparatus is marketed by the Burgess-Parr Company.

The development of modern micro-methods has led to the devising of a number of pieces of apparatus for the determination of the number of double bonds in the molecule of a substance by the hydrogenation of a few milligrams of material. Smith (*J. Biol. Chem.* 1932, 96, 35) devised an apparatus in which the uptake of hydrogen was measured directly by the diminution in volume under constant pressure; an improvement of this apparatus by Jackson and Jones (*J.C.S.* 1936, 895; *cf.* Jackson, *Chem. and Ind.* 1938, 57, 1076) is extensively used to-day. The other widely used apparatus is that of Kuhn and Möller (*Angew. Chem.* 1934, 47,

145) in which the difference in volume between the hydrogen taken up by the substance and that taken up by a control substance is measured. Adams' platinum oxide catalyst (*see below*) is the catalyst generally employed in these experiments, the solvent being, usually, acetic acid, decalin or methylcyclohexane.

**Catalysts.**—(1) *Platinum Catalysts.*—Of the platinum catalysts in use to-day by far the most popular is platinum black produced by reduction, in the hydrogenation vessel, of platinum oxide prepared by the method of Adams, Voorhees and Shriner (*Organic Syntheses*, 1928, 8, 92). This "Adams' catalyst" is prepared by fusing chloroplatinic acid with sodium nitrate at 500–550°. After use it may be re-worked by solution in *aqua regia* followed by evaporation and fusion with sodium nitrate; if extensively poisoned it may be necessary to purify it by conversion into ammonium chloroplatinate (Balde-schweiler and Mikeska, *J. Amer. Chem. Soc.* 1935, 57, 977) which can then be used directly for the fusion with sodium nitrate (Bruce, *Organic Syntheses*, 1937, 17, 98; *J. Amer. Chem. Soc.* 1936, 58, 687). Cook and Linstead (*J.C.S.* 1934, 952) recommend the use of potassium, instead of sodium, nitrate in the fusion and consider that a more active catalyst is obtained in this way. Short (*J.S.C.I.* 1936, 55, 14T) describes a special apparatus for carrying out the fusion. The following simplified procedure has been found to give consistently good results:

One gram of commercial chloroplatinic acid is dissolved in 3 c.c. of water in a porcelain crucible and to the solution is added 10 g. of pure sodium nitrate. The mixture is evaporated to dryness over a small flame with stirring. The full heat of the Bunsen flame is then applied to the crucible and vigorous stirring is continued until the mass is completely molten and the initial vigorous decomposition, which is accompanied by frothing, has abated. The flame is then regulated so that the base of the crucible is at a dull red heat and this temperature is maintained, without stirring, for 30 minutes. The cooled product is extracted with hot water, filtered and the brown oxide washed well with hot water and dried in a vacuum desiccator. The yield is almost theoretical.

Loew (*Ber.* 1890, 23, 289) prepared platinum black by the reduction of platinum chloride with formaldehyde in the presence of sodium hydroxide. Many modifications of this method have been described of which the following (Willstätter and Waldschmidt-Leitz, *ibid.* 1921, 54 [B], 121) seems to give a very active catalyst:

Eight c.c. of a solution of chloroplatinic acid, prepared from 2 g. of platinum and containing some hydrochloric acid, are mixed with 13 c.c. of formalin. After cooling to  $-10^{\circ}$ , 42 g. of 50% potassium hydroxide solution are added dropwise with stirring, the temperature being kept below  $5^{\circ}$ . When the addition is complete the product is stirred at  $55-60^{\circ}$  for 30 minutes. The platinum black is then washed by decantation (best in a cylinder), until the washings are neutral and free from chloride. It is then filtered off, care being taken to keep it covered with water, lightly pressed between filter papers and

dried in a vacuum desiccator. Access of air to the catalyst must be avoided.

(2) *Palladium Catalysts*.—Palladium black may be prepared by methods analogous to those described above for platinum black; thus Shriner and Adams (J. Amer. Chem. Soc. 1927, **49**, 1093) fuse palladous chloride with sodium nitrate and Zelinsky and Glinka (Ber. 1911, **44**, 2309) reduce palladous chloride with potassium formate.

Usually, however, palladium is deposited on an inert carrier. For this purpose charcoal (Mannich and Thiele, Arch. Pharm. 1915, **253**, 183), barium sulphate (Schmidt, Ber. 1919, **52** [B], 409) and alkaline-earth carbonates (Busch and Stove, *ibid.* 1916, **49**, 1064) have found extensive application. For the preparation of palladised charcoal, palladous chloride is dissolved in warm concentrated hydrochloric acid; the requisite amount of active charcoal (previously purified by boiling with hydrochloric acid) is added to the diluted solution and the whole is stirred or shaken in hydrogen with the addition of some sodium acetate. The palladised charcoal may either be filtered off and stored in a desiccator or used directly. Zelinski, Packendorff and Leder-Packendorff (*ibid.* 1933, **66** [B], 872; cf. Robinson and Koebner, J.C.S. 1938, 1996) prepare a selective catalyst by depositing both platinum and palladium on active charcoal. Of the other carriers strontium carbonate gives an excellent robust catalyst suitable for general use. For the preparation of 2% palladised strontium carbonate, 30 g. of strontium carbonate are suspended in 500 c.c. of water at 70°. A solution of 1 g. of palladous chloride in a little warm concentrated hydrochloric acid is stirred in. After stirring at 70° for a few minutes the catalyst is filtered off, washed, dried in the steam-oven and stored; it is reduced, as required, in the hydrogenation vessel.

(3) *Colloidal Platinum and Palladium Catalysts*.—Paal and his co-workers (Ber. 1904, **37**, 124; 1905, **38**, 1401; 1908, **41**, 805) developed a catalyst which consists of a colloidal solution of platinum or palladium protected by "sodium lysalbate," a product of the alkaline hydrolysis of egg albumen; this catalyst can only be used in neutral or alkaline solution, since the protective colloid is sensitive to acid.

Skita and his co-workers (*ibid.* 1909, **42**, 1627; 1911, **44**, 2862; 1912, **45**, 3579, 3589) use gum arabic as the protective colloid. A solution of palladous chloride containing gum arabic is added to a solution of the substance to be hydrogenated in alcohol or acetic acid. The catalyst is formed by shaking in hydrogen, after which the hydrogenation proceeds in the usual way. Recently these colloidal catalysts have fallen into disfavour owing to the greater robustness of such non-colloidal catalysts as Adams' platinum oxide and palladised charcoal or strontium carbonate.

(4) *Nickel Catalysts*.—The outstanding nickel catalyst for hydrogenation in the liquid phase is Raney nickel, which has no serious rival among nickel catalysts for this purpose. Raney (U.S.P. 1628190) prepared his catalyst by the action of sodium hydroxide on a nickel-

aluminium alloy of the composition  $\text{Al}_2\text{Ni}$ . This catalyst has been much used by Adkins and his co-workers in connection with the high-pressure hydrogenator mentioned above; the following more active preparation is due to Covert and Adkins (J. Amer. Chem. Soc. 1932, **54**, 4116).

Finely-ground nickel-aluminium alloy (300 g.) is added over 2-3 hours to 300 g. of sodium hydroxide in 1,200 c.c. of distilled water in a 4 litre beaker surrounded by ice. The mixture is then heated for 4 hours to 115-120° with occasional stirring. A further 400 c.c. of 19% sodium hydroxide solution is then added and the mixture kept at 115-120° until no more hydrogen is evolved (about 3 hours). After dilution to 3 litres the nickel is washed 6 times with water by decantation and then alternately by suspension and by washing on a Buchner funnel until the filtrate is neutral to litmus. The nickel (which is pyrophoric when dry) is then washed 3 times with 95% alcohol and stored under alcohol in glass-stoppered bottles. Raney nickel may retain about 17% of alcohol, which may lead to ester formation in the hydrogenation of acids, but it may be removed by storage for some hours under ether or methylcyclohexane (McClellan and Connor, *ibid.* 1941, **63**, 484). The outstanding characteristic of Raney nickel is its activity as compared with other nickel catalysts. Lieber and Smith (*ibid.* 1936, **58**, 1417) enhance its activity by adding a small amount of platinum chloride at the commencement of the hydrogenation. Paul and Hilly (Compt. rend. 1938, **206**, 608) prepared an iron catalyst, said to be specific for the semi-hydrogenation of acetylenic linkages, by a similar process with an iron-aluminium alloy; they have also described a modified process for the preparation of Raney nickel (Bull. Soc. chim. 1936, [v], 3, 2330).

Adkins has also used a nickel-kieselguhr catalyst produced by treatment of kieselguhr with nickel nitrate and ammonium carbonate followed by reduction at 450° (Covert, Connor and Adkins, J. Amer. Chem. Soc. 1932, **54**, 1651); this catalyst is less active than Raney nickel. Sully (Chem. and Ind. 1939, **58**, 282) prepares an active catalyst by precipitation of nickel carbonate from nickel sulphate by means of sodium carbonate; the precipitate is washed carefully and reduced in hydrogen. It is claimed that this catalyst (5%) will hydrogenate crotonaldehyde to butyl alcohol in 5 hours at 80°/200 lbs.

(5) *Other Catalysts*.—Among the many other catalysts described in the literature the only one whose action has been generally studied is "copper chromite" (Connor, Folkers and Adkins, *ibid.* 1931, **53**, 2012; 1932, **54**, 1138). In these two papers procedures for the preparation of a wide range of copper chromite catalysts are described; the most active are made by adding ammonia to a mixture of copper nitrate, barium nitrate and ammonium dichromate and igniting the precipitate. Adkins and Connor (*ibid.* 1931, **53**, 1091) specially recommend copper chromite for the hydrogenation of carbonyl compounds to alcohols, of benzyl alcohols to hydrocarbons, nitro-groups to amines and for

the selective hydrogenation of double bonds. Pyridine nuclei are readily hydrogenated but the catalyst is inactive towards cyano-groups and benzene nuclei. It is not so easily poisoned as nickel and is best used at high pressures.

Fauconneau (Bull. Soc. chim. 1937, [v], 4, 58, 63) has prepared active copper and cobalt catalysts by the action of sodium hydroxide on Devarda's alloy and the alloy  $\text{Co}_2\text{Al}_5$ , respectively.

**Solvents.**—The most widely used hydrogenation solvents are ethyl alcohol, acetic acid, ethyl acetate, ether, and saturated hydrocarbons such as *n*-hexane, decalin and cyclohexane. It is generally considered that acetic acid is the most useful solvent from the point of view of rapidity of hydrogenation (Willstätter and Hatt, Ber. 1912, 45, 1471; Skita and Meyer, *ibid.* 1912, 45, 3500); it is specially useful for the hydrogenation of aromatic nuclei (Adams and Marshall, J. Amer. Chem. Soc. 1928, 50, 1970). Carothers and Adams (*ibid.* 1924, 46, 1675) investigated the hydrogenation of aldehydes in a variety of solvents but came to no very definite conclusions. Maxted and Stone (J.C.S. 1938, 454), working with erotonic acid and platinum, were unable to correlate the rate of hydrogenation (corrected for the vapour pressure of the solvent) with any other property of the solvent.

**Experimental Conditions.**—In general, increase of temperature leads to an increase in the rate of hydrogenation, but this effect is masked by the lowering of the partial pressure of hydrogen in the reaction vessel consequent on the rise in the vapour pressure of the solvent; it is thus necessary to determine the optimum temperature for each case experimentally. The rate of hydrogenation usually increases with increasing pressure, but here again no general rule as to the magnitude of the pressure effect can be given. The effect of pressure is particularly marked with nickel catalysts, with which there seems to be an optimum pressure for many hydrogenations (cf. Adkins, Cramer and Connor, J. Amer. Chem. Soc. 1931, 53, 1402). In many cases increase of pressure has been shown to give rise to the formation of a different product (Skita, Ber. 1915, 48, 1486; Skita and Ritter, *ibid.* 1910, 43, 3393). The amount of catalyst used has also an important effect. Within limits the rate of hydrogenation increases with an increase in the amount of catalyst added (cf. Paal and Schwartz, *ibid.* 1915, 48, 994; Bourguet, Gredy and Roubach, Bull. Soc. chim. 1931, [iv], 49, 897). Another factor influencing the rate of hydrogenation is the vigour of the shaking or stirring.

It frequently happens that a catalytic hydrogenation comes to a standstill short of completion; in such cases the catalyst may often be re-activated by shaking or stirring with air or oxygen. In specially difficult cases hydrogenation may be effected by boiling the substance with an excess of tetralin in the presence of palladium black or palladised charcoal, the tetralin being dehydrogenated to naphthalene (Kindler and Peschke, Annalen, 1932, 497, 193; 1933, 501, 191).

**Poisons and Promoters.**—The literature on catalyst poisons is both large and chaotic. In

general, mercury compounds are regarded as poisons (Paal and Hartmann, Ber. 1918, 51, 711); nevertheless the presence of a small amount of metallic mercury in the hydrogenation vessel seems to have little adverse effect, at any rate with palladised charcoal and Adams' catalyst. Compounds of sulphur (including vulcanised rubber), arsenic compounds and hydrogen cyanide are also stated to be poisons (Hinrichsen and Kempf, *ibid.* 1912, 45, 2107; Busch and Stove, *ibid.* 1916, 49, 1070; Kelber, *ibid.* 1916, 49, 1868); for this reason Adams and Voorhees (Organic Syntheses, 1928, 8, 14) recommend that rubber tubing and stoppers used in apparatus for catalytic hydrogenation should be boiled out with 20% sodium hydroxide and then with water. However, Truffault, in a study of poisoning in catalytic hydrogenation (Bull. Soc. chim. 1935, [v], 2, 244), found vulcanised rubber to be ineffective as a poison. Unsaturated substances obtained by dehydration by means of thionyl chloride are frequently resistant to hydrogenation owing to the presence of small amounts of sulphur compounds; treatment with a little aluminium amalgam in moist ether frequently brings about the removal of these impurities (cf. Gaubert, Linstead and Rydon, J.C.S. 1937, 1977). Partial poisoning of the catalyst may be of value in increasing its selectivity; thus a partially poisoned catalyst is used in the Rosenmund hydrogenation of acid chlorides to aldehydes (p. 359a). Maxted and Morrish (*ibid.* 1940, 252) find that, in the case of elements such as sulphur, selenium, tellurium and phosphorus, the catalytic toxicity generally disappears if the normally poisonous atom is associated with a completely shared octet of electrons.

Adams and his co-workers (J. Amer. Chem. Soc. 1923, 45, 1071, 3029; 1924, 46, 1675; 1925, 47, 1047, 1098, 1147, 3061; 1926, 48, 477) found that the addition of certain inorganic salts affected the rate of hydrogenation; iron salts, especially, markedly increase the rate of hydrogenation of aldehydes.

Many authors have noted the effect of mineral acids in small amount in speeding up hydrogenation (Kindler, Brandt and Gehlhaar, Annalen, 1934, 511, 209; Kindler and Peschke, *ibid.* 1935, 519, 291; Brown, Durand and Marvel, J. Amer. Chem. Soc. 1936, 58, 1594), and a recent study shows that the hydrogenation of benzene with platinum black is markedly dependent on  $p_{\text{H}}$ , being fastest in acid, and almost stopped in alkaline solution (Foresti, Gazzetta, 1936, 66, 455, 464). Peroxides, such as benzoyl peroxide and perbenzoic acid, have also been found to increase the velocity of catalytic hydrogenations (Thomson, J. Amer. Chem. Soc. 1934, 56, 2744).

**General Considerations.**—Owing to the vastly different characters of the available catalysts it is not possible to place them in any definite order of effectiveness. For laboratory hydrogenation the catalysts in greatest favour are Adams' platinum oxide catalyst, palladised strontium carbonate or charcoal, and Raney nickel. The most favoured solvents are ethyl alcohol and acetic acid.

The effect of constitution on ease of hydrogenation

tion follows no very general rules, but the hydrogenation of aromatic nuclei is more difficult than that of ethylenic and acetylenic linkages and carbonyl groups. Among ethylenic compounds it has been observed by many workers that the rate of hydrogenation decreases with the accumulation of alkyl groups on the unsaturated carbon atoms (*cf.* Vavon *et al.*, *Compt. rend.* 1923, 176, 898; 177, 401, 453; Lebedev, Kobliansky and Yakubchik, *J.C.S.* 1925, 127, 417). It has been observed that the cyclopentane ring is sometimes opened in hydrogenations at high temperatures (Zehnski, Kazanski and Plate, *Ber.* 1933, 66 [B], 1415; 1935, 68 [B], 1869; Denisenko, *ibid.* 1936, 69 [B], 1353, 1668, 2183).

Paal and Schiedewitz (*ibid.* 1927, 60 [B], 1221; 1930, 63 [B], 766; Paal, Schiedewitz and Rauscher, *ibid.* 1931, 64 [B], 1521) state that, in general, the *cis*-forms of ethylenic compounds are more rapidly hydrogenated than the *trans*; Weygand, Werner and Lanzendorf (*J. pr. Chem.* 1938, [ii], 151, 231), however, find that this conclusion is not universally valid. According to Bourguel and Yvon (*Compt. rend.* 1926, 182, 224) the partial hydrogenation of acetylenic compounds yields *cis*-ethylenic compounds. A stereochemical conclusion which is much more general is the now classical Auwers-Skita rule (Skita, *Ber.* 1920, 53 [B], 1792; von Auwers, *Annalen*, 1920, 420, 84) which states that hydrogenation in neutral or alkaline solution favours the formation of *trans*-compounds, whereas hydrogenation in acid media leads to *cis*-compounds. This rule has proved of great value in the assignment of configurations to many products but its interpretation is, in certain cases, rather doubtful (Ruzicka, Brungger, Eichenberger and Meyer, *Helv. Chim. Acta*, 1934, 17, 1407).

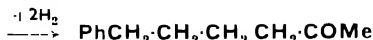
In a recent review (*Chem. Soc. Annual Rep.* 1937, 34, 221) Linstead remarks that "Hydrogenation of unsaturated compounds over platinum or palladium catalysts is now part of standard technique. By the improvement in the activity of catalysts . . . it has become possible to hydrogenate almost any description of double bond, the operation being carried out in the liquid phase or in solution at the ordinary temperature and at the ordinary or very slightly raised pressure. . . . Complete hydrogenation has thus largely become a matter of routine, and the main developments must now be in the improvement of selectivity." Several examples of selective hydrogenation will be discussed later, but certain results may be mentioned here. Dupont (*Bull. Soc. chim.* 1936, [v], 3, 1021, 1030) found that Raney nickel was generally more selective in its action than Adams' catalyst; in the hydrogenation of polyenes with this catalyst stepwise reduction was the rule as it was in the case of acetylenes. Similar results were, however, obtained by Bourguel (*Bull. Soc. chim.* 1927, [iv], 41, 1446) with a platinum catalyst. The work of Adkins on high pressure hydrogenation with Raney nickel and copper chromite has led to the possibility of achieving remarkably selective hydrogenation. Thus, since copper chromite is inactive to benzene nuclei, whereas Raney nickel is inert towards ester groups, it is

possible to hydrogenate one and the same aromatic ester to an aromatic alcohol, with copper chromite, or to a cyclohexane ester, with Raney nickel. A most remarkable selective hydrogenation is the reduction of butyl oleate to the corresponding unsaturated octadecanol using a zinc-chromium oxide catalyst (Saur and Adkins, *J. Amer. Chem. Soc.* 1937, 59, 1).

### SPECIAL.

The remainder of this article deals, in detail, with the hydrogenation of various important classes of compound.

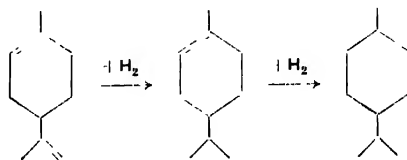
**Ethylenic Compounds.**—In general carbon-carbon double bonds are readily hydrogenated even with comparatively inert catalysts; carboxyl groups do not interfere and it is generally possible, by correctly choosing the experimental conditions, to hydrogenate the ethylenic linkage in an unsaturated carbonyl compound without affecting the carbonyl groups (*cf.* Skita, *Ber.* 1908, 41, 2938; Skita and Ritter, *ibid.* 1910, 43, 3393; Paal, *ibid.* 1912, 45, 2221; Vavon, *Ann. chim.* 1914, [ix], 1, 193). A useful table showing the relative ease of hydrogenation (Adams' catalyst) of a wide range of ethylenic compounds is given by Kern, Shriner and Adams (*J. Amer. Chem. Soc.* 1925, 47, 1147); attention has already been drawn to the fact that the rate of hydrogenation of an ethylenic linkage is reduced by the accumulation of substituents (*cf.* Zartman and Adkins, *ibid.* 1932, 54, 1668; Lebedev and Platonov, *J.C.S.* 1930, 321). Paal (*Ber.* 1912, 45, 2221) studied the stepwise hydrogenation of a series of dienic compounds; he concluded that stepwise hydrogenation only occurred when the double bonds were separated by at least 1 carbon atom, thus:



but



Similar phenomena are observed with terpene derivatives (*cf.* Wallach, *Annalen*, 1911, 381, 51), *e.g.* limonene:



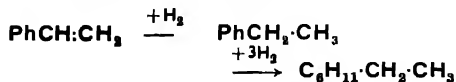
If a relatively inactive catalyst is used it is frequently possible to obtain good yields of the pure mono-unsaturated compound in this way (*e.g.* caryophyllene  $\rightarrow$  dihydrocaryophyllene; Deussen, *ibid.* 1912, 388, 156; *J. pr. Chem.* 1926, [ii], 114, 83).

**Acetylenic Compounds** are usually very readily hydrogenated under mild conditions. Two-stage hydrogenation:

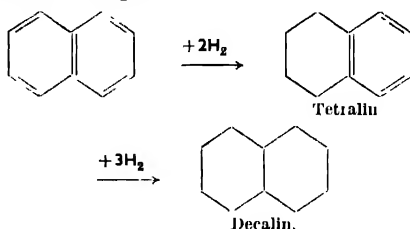


has frequently been observed, especially with palladium catalysts (*cf.* Paal *et al.*, Ber. 1909, 42, 3930; 1915, 48, 1202; Kelber and Schwartz, *ibid.* 1912, 45, 1946; Bourguet, Bull. Soc. chim. 1927, [iv], 41, 1475). Platinum catalysts are not so effective in bringing about this partial hydrogenation, mixtures of saturated and ethylenic compounds being produced (Paal and Schwartz, Ber. 1918, 51, 640; Salkind *et al.*, J. Russ. Phys. Chem. Soc. 1914, 45, 1875; 1917, 49, 130; Ber. 1933, 66 [B], 321; J. Gen. Chem. U.S.S.R. 1933, 3, 91; 1936, 6, 1085; 1937, 7, 740, 1235). Raney nickel (Dupont, Bull. Soc. chim. 1936, [v], 3, 1030; Campbell and O'Connor, J. Amer. Chem. Soc. 1939, 61, 2897) and the iron catalyst prepared similarly (Paul and Hilly, Compt. rend. 1938, 206, 608; Thompson and Watt, J. Amer. Chem. Soc. 1940, 62, 2555) are effective catalysts for the semi-hydrogenation of acetylenes. U.S.P. 1920242 describes the partial hydrogenation of vinylacetylene to butadiene. Bourguet (Compt. rend. 1925, 180, 1753) finds that the hydrogenation of acetylenic compounds with colloidal palladium at low temperatures usually yields the *cis*-form of the ethylenic product.

**Aromatic Nuclei.**—The hydrogenation of the benzene nucleus is a more difficult process than that of the ethylenic double-bond; it is best brought about with a platinum catalyst in acetic acid solution (Willstätter and Hatt, Ber. 1912, 45, 1471; Skita and Meyer, *ibid.* 1912, 45, 3589). Adams and Marshall (J. Amer. Chem. Soc. 1928, 50, 1972) give a useful table of the relative rates of hydrogenation of a range of aromatic compounds with Adams' catalyst in acetic acid. Copper chromite is not effective for the hydrogenation of aromatic nuclei, but benzene and its homologues are hydrogenated over Raney nickel at 120–175°/100 atm.; the accumulation of phenyl groups renders hydrogenation more difficult (Adkins, Zartman and Cramer, *ibid.* 1931, 53, 1425; Zartman and Adkins, *ibid.* 1932, 54, 1668). Benzenoid compounds are also fairly readily hydrogenated by the method of Sabatier and Senderens (Compt. rend. 1901, 132, 210, 566, 1254); in the case of compounds containing several isolated benzene nuclei it is possible to hydrogenate these successively (Sabatier and Murat, *ibid.* 1912, 154, 1390, 1771; 155, 385; Godchot, *ibid.* 1908, 147, 1057). It is interesting to note that, whereas most diphenyl derivatives can be hydrogenated normally, certain compounds which are optically active owing to restricted rotation are very resistant to hydrogenation (Waldeland, Zartman and Adkins, J. Amer. Chem. Soc. 1933, 55, 4234). Willstätter and King (Ber. 1913, 46, 527), using platinum black, brought about the hydrogenation of styrene in two stages:



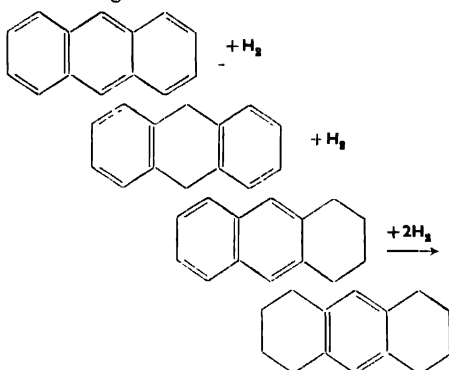
Sabatier and Senderens (Compt. rend. 1901, 132, 1257) succeeded in hydrogenating naphthalene to tetrahydronaphthalene (tetralin); Leroux (*ibid.* 1904, 139, 672), using more drastic conditions, converted this into decahydronaphthalene (decalin). Using a nickel catalyst at 250°/120 atm., Ipatiev (Ber. 1907, 40, 1281) brought about the two-stage hydrogenation of naphthalene:



Willstätter and his co-workers made a careful study of the hydrogenation of naphthalene over platinum black in acetic acid; they were able to demonstrate the successive formation of the dihydro-, tetrahydro- and decahydro-compounds (*ibid.* 1912, 45, 1471; 1913, 46, 527). Willstätter and Seitz (*ibid.* 1924, 57 [B], 683) showed that the decalin so obtained was the pure *cis*-compound, whereas nickel at 160° yields chiefly *trans*-decalin. The most important work on the hydrogenation of naphthalene is probably that of Schroeter (Annalen, 1922, 426, 1) who worked out a method, using a nickel catalyst at 200°/12–15 atm., for the production of tetralin in large quantities. Since naphthalene is produced as a by-product in quantities greatly in excess of requirements, its hydrogenation to useful solvents has become of great technical importance (B.P. 147474, 147476, 147580, 147747, 172688, 322445; U.S.P. 1733908, 1733909; G.P. 299012, 324861, 324862, 324863; *cf.* B.P. 304403). Musser and Adkins (J. Amer. Chem. Soc. 1938, 60, 664) find that naphthalene may be hydrogenated to tetralin over Raney nickel at 100°; with copper chromite a higher temperature (200°) is required, but the reaction stops completely at the tetralin stage. Lush (J.S.C.I. 1927, 46, 454T) finds that, with a nickel catalyst, vapour-phase hydrogenation of naphthalene yields exclusively tetralin, while decalin is produced in liquid-phase hydrogenation; he suggests that this is due to a difference in orientation at the catalytic surface in the two phases. On the other hand, Maillard (Compt. rend. 1933, 197, 1422) finds that, in the liquid phase, decalin is produced directly at 20°, whereas tetralin forms an intermediate product at all temperatures above 60°.

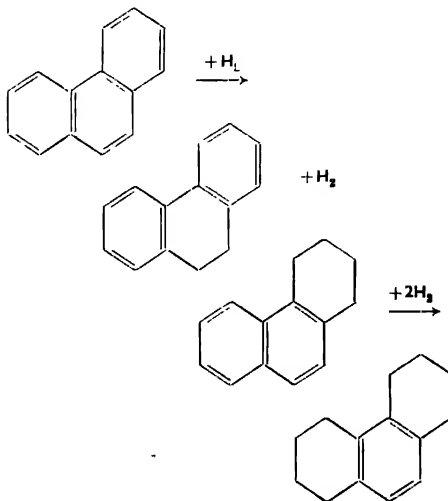
Godchot (Ann. Chim. Phys. 1907, [viii], 12, 468; Bull. Soc. chim. 1907, [iv], 1, 724) observed stepwise hydrogenation of anthracene to tetrahydro-, octahydro- and perhydro-anthracenes in the vapour phase over an active nickel catalyst, and similar results were obtained by pressure hydrogenation (Ipatiev, Jakovlev and Rakitin, Ber. 1908, 41, 996). Schroeter (*ibid.* 1924, 57 [B], 2003) found that anthracene undergoes hydrogenation with a nickel catalyst at 120–

150°/10–20 atm., to the octahydro-compound in three stages :



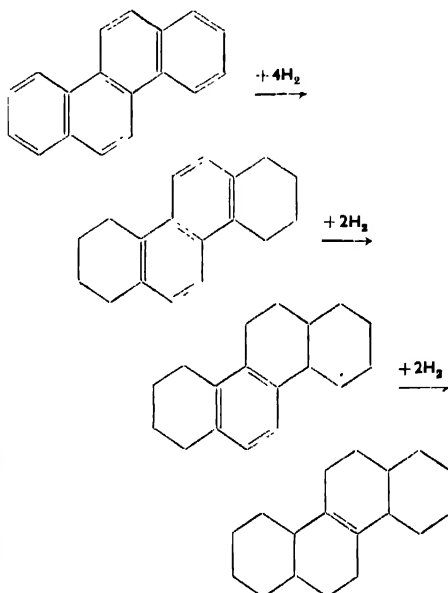
Fries, Schilling and Littmann (*ibid.* 1932, 65 [B], 1494) state that the 1:2:3:4-tetrahydro-compound is formed by two simultaneous reactions, viz. a slow reaction through the 9:10-dihydride and a fast direct reaction. Further hydrogenation yields perhydroanthracene, which is obtained in different stereoisomeric forms according to the catalyst and solvent used. Martin and Hugel (Bull. Soc. chim. 1933, [iv], 53, 1500) have, however, brought forward evidence in support of Schroeter's view of the course of the reaction. According to Waterman, Leendertse and Cranendonk (Rec. trav. chim. 1939, 58, 83) hydrogenation of anthracene over a nickel-kieselguhr catalyst yields first octahydroanthracene and then a mixture of perhydroanthracenes.

The earlier results on the hydrogenation of phenanthrene (Breteau, Compt. rend. 1905, 140, 942; Schmidt and Metzger, Ber. 1907, 40, 4240; Ipatiev, Jakovlev and Rakitin, *ibid.* 1908, 41, 996; Schmidt and Fischer, *ibid.* 1908, 41, 4252; Padoa and Fabris, Gazzetta, 1909, 39, 333) are somewhat conflicting. It was shown, however, by Schroeter (Ber. 1924, 57 [B], 2025; Schroeter, Müller and Huang, *ibid.* 1929, 62 [B], 645) that the reaction took the following course :



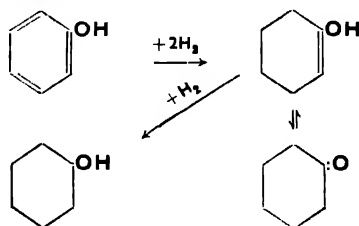
The symmetrical octahydride can be prepared in good yield by this method (van de Kamp and Mosettig, J. Amer. Chem. Soc. 1935, 57, 1107); recently Durland and Adkins (*ibid.* 1937, 59, 135) working with Raney nickel and copper chromite, have shown that, by varying the experimental conditions, considerable amounts of the unsymmetrical octahydride may be obtained. The pure 9:10-dihydride may be prepared in quantity by selective hydrogenation using a special copper chromite catalyst (Burger and Mosettig, *ibid.* 1935, 57, 2731; 1936, 58, 1857).

J. von Braun and Irmisch (Ber. 1932, 65 [B], 883) found that chrysene is hydrogenated over a nickel catalyst in three stages :



These workers were unable to obtain the perhydro-compound, but Spilker (Angew. Chem. 1935, 48, 368) succeeded in preparing this by using specially pure chrysene in decalin solution.

**Benzene Derivatives.**—According to the conditions, a phenol may be hydrogenated either to the corresponding cyclohexanol or to the cyclohexanone :



The initial formation of the enolic form of the cyclohexanone postulated in the above scheme has been substantiated by the work of Grignard and Mingasson (Compt. rend. 1927, 185, 1552).

In the vapour-phase hydrogenation of phenol over nickel, Sabatier and Senderens (*ibid.* 1903, 137, 1027) found that the amount of cyclohexanone formed increased with rise of temperature. The mixture formed from phenol by hydrogenation at 180° may be converted into pure cyclohexanol by rehydrogenation with nickel at 150–170° and into pure cyclohexanone by dehydrogenation over copper at 330° homologues behave similarly (Sabatier and Mailhe, *ibid.* 1905, 140, 350; 1906, 142, 553) Willstätter and Hatt (Ber. 1912, 45, 1471) using platinum black in acetic acid, obtained a mixture of cyclohexanol and cyclohexanone from phenol; however, a convenient laboratory method for the hydrogenation of phenol to cyclohexanol with Adams' catalyst in acetic acid has been described (Adams and Voorhees, J. Amer. Chem. Soc. 1922, 44, 1404). Broche (Compt. rend. 1922, 175, 583; Bull. Soc. chim. 1922, [iv], 31, 1270) studied the pressure hydrogenation of a number of phenols to the corresponding cyclohexanols over nickel. In recent years cyclohexanone (*q.v.*) ("Sextone") and cyclohexanol (*q.v.*) ("Sextol"; "Hexalin") and their homologues have become technically important as inexpensive solvents and large quantities are produced by the hydrogenation of phenol and the cresols (U.S.P. 1247629, 1643619; G.P. 444665, 473960). The hydrogenation of polyphenols is not generally very satisfactory (Sabatier and Senderens, Ann. Chim. Phys. 1905, [viii], 4, 428; Sabatier and Mailhe, Compt. rend. 1908, 146, 1193; Ipatiev and Lougovoy, J. Russ. Phys. Chem. Soc. 1914, 46, 470; Wieland and Wishart, Ber. 1914, 47, 2082; Von Braun, Haensel and Zobel, Annalen, 1928, 462, 283).

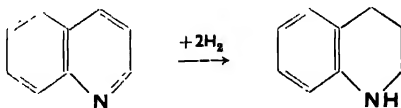
$\alpha$ - and  $\beta$ -Naphthols on reduction over nickel at 130° give 85% and 75% respectively of the 1:2:3:4-tetrahydro-derivative and 15% and 25% respectively of the 5:6:7:8-tetrahydro-derivative (Brochet and Cornubert, Compt. rend. 1921, 172, 1499; Bull. Soc. chim. 1922, [iv], 31, 1280). Schroeter (Annalen, 1922, 426, 83) obtained large amounts of  $\alpha$ -tetralone and of tetralin in the hydrogenation of  $\alpha$ -naphthol at 200°; at lower temperatures  $\alpha$ -tetralone was the chief product. With  $\beta$ -naphthol less de-oxygenation was observed (*cf.* Huckel, *ibid.* 1927, 451, 109). Complete hydrogenation of the naphthols yields  $\alpha$ - and  $\beta$ -decalols (Leroux, Compt. rend. 1905, 141, 953; Ann. Chim. Phys. 1910, [viii], 21, 483; Ipatiev, Ber. 1907, 40, 1281; G.P. 444665).

Sabatier and Murat (Compt. rend. 1912, 154, 923) were unable to hydrogenate benzoic acid with nickel at 170–180° but found that benzoic esters were readily converted into the cyclohexane derivatives. Ipatiev and his co-workers (Ber. 1908, 41, 1001; 1926, 59 [B], 306) were able to bring about the smooth hydrogenation of the alkali salts of aromatic acids by using nickel under pressure. This method is to be preferred when the vapour-phase hydrogenation of the ester is accompanied by decarboxylation; thus, diethyl phthalate yields carbon dioxide and the esters of phthalic and benzoic acids, whereas potassium phthalate gives potassium cyclohexane-1:2-dicarboxylate in good yield (Ipatiev

and Philipev, *ibid.* 1908, 41, 1001). Skita and Meyer (*ibid.* 1912, 45, 3589) were able to hydrogenate benzoic acid successfully with colloidal palladium in acetic acid, and Willstätter and Jaquet (*ibid.* 1918, 51, 767) studied the hydrogenation of several aromatic acids with platinum black in acetic acid; the latter authors noticed the interesting fact that hydrogenation was rendered very much more difficult by the presence of even small traces of the acid anhydride. The hydrogenation of ethyl benzoate with Adams' catalyst in ethyl alcohol has been described by Gray and Marvel (J. Amer. Chem. Soc. 1925, 47, 2799). The presence of a hydroxyl group appears to facilitate the hydrogenation of aromatic acids; thus, Balas and Šröl (Coll. Czech Chem. Comm. 1929, 1, 685; *cf.* Edson, J.S.C.I. 1934, 53, 1387) were able to hydrogenate hydroxybenzoic acids under very mild conditions.

The hydrogenation of aromatic amines is complicated by the formation of by-products. Thus Sabatier and Senderens (Compt. rend. 1904, 138, 457, 1257) found that, in the vapour-phase hydrogenation of aniline over nickel, not only was cyclohexylamine formed by the normal reaction, but the secondary amines dicyclohexylamine and cyclohexylaniline were also produced, ammonia being eliminated. The same side-reactions are observed with other catalysts, *e.g.* nickel under pressure (Ipatiev, Ber. 1908, 41, 991), Willstätter's platinum black (Willstätter and Hatt, *ibid.* 1912, 45, 1471). This type of side-reaction does not occur with *sec*- and *tert*-aromatic amines (Sabatier and Senderens, *ibid.* 1904, 138, 1257; Darzens, *ibid.* 1909, 149, 1001). Adam's catalyst has been used successfully in the hydrogenation of aromatic amines (Hiers and Adams, *ibid.* 1926, 59 [B], 162).

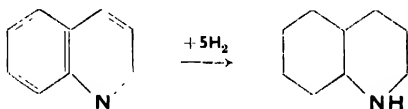
**Heterocyclic Compounds.**—The hydrogenation of many heterocyclic compounds by the Sabatier-Senderens technique is unsatisfactory owing to ring-fission, but Darzens (Compt. rend. 1909, 149, 1001) successfully hydrogenated quinoline over nickel at 160–180° to the 1:2:3:4-tetrahydro-derivative.



Pressure hydrogenation has also been employed successfully (Von Braun, Petzold and Seemann, Ber. 1922, 55 [B], 3779; Sadikov and Mikhailov, *ibid.* 1928, 61 [B], 421, 1797; J.C.S. 1928, 438); the nature of the product is dependent on the nature and position of the substituents (Von Braun *et al.*, Ber. 1923, 56 [B], 1338, 1347). Platinised asbestos appears to be a specially useful catalyst for the hydrogenation of pyridine to piperidine (Zelinsky and Borisoff, *ibid.* 1924, 57 [B], 150). The hydrogenation of a large number of pyridine and quinoline derivatives with colloidal palladium was studied by Skita and his co-workers (*ibid.* 1912, 45, 3312, 3579; 1916, 49, 1597; 1924, 57 [B], 977); gum arabic was used as the protective

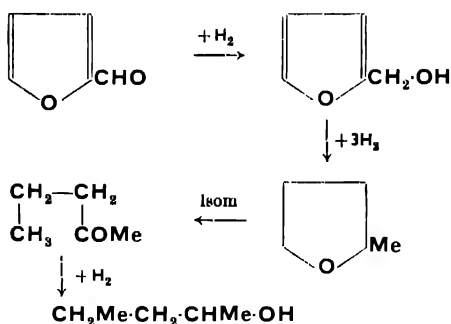


colloid and the presence of acetic acid was advantageous except in the case of pyridine which was best hydrogenated in the presence of hydrochloric acid. Adams' platinum oxide catalyst is not effective for the hydrogenation of free pyridine, but the hydrochloride is readily hydrogenated in alcoholic solution (Hamilton and Adams, *J. Amer. Chem. Soc.* 1928, **50**, 2260). Using colloidal platinum, quinoline has been hydrogenated to a mixture of stereoisomeric decahydro-compounds:



(Huckel and Stepf, *Annalen*, 1927, **453**, 163; Lehmstedt, *Ber.* 1927, **60** [B], 1370). Recently, Raney nickel has been found to be an excellent catalyst for the hydrogenation of pyridine and its derivatives (Adkins and Connor, *J. Amer. Chem. Soc.* 1931, **53**, 1091; Adkins, Kuick, Farlow and Wojcik, *ibid.* 1934, **56**, 2425), substituents in the 2- and 6- positions facilitating the hydrogenation; a special palladised nickel catalyst has also been recommended (Ushakov, Livshitz and Zhdanova, *Bull. Soc. chim.* 1935, [v], **2**, 573). M. De Jong and Wibaut (*Rec. trav. chim.* 1930, **49**, 237) used Adams' catalyst in acetic acid for the hydrogenation of pyrroles to pyrrolidines and observed that substitution facilitated hydrogenation; a similar observation has been made with Raney nickel (Signaigo and Adkins, *J. Amer. Chem. Soc.* 1936, **58**, 709; Rainey and Adkins, *ibid.* 1939, **61**, 1104).

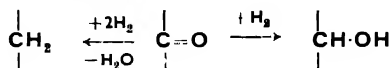
The hydrogenation of furfural in the vapour-phase over nickel is a complicated process, the following reactions taking place:



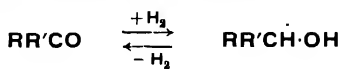
(Padua and Ponti, *Atti R. Accad. Lincei*, 1906, **15**, (ii), 610; *cf.* F.P. 639756). Scheibler, Sotasek and Friese (*Ber.* 1924, **57**, 1443) attempted to hydrogenate furfural to tetrahydrofurfural; in order to protect the aldehyde group they employed the diethylacetal and the diacetate, of which only the latter gave satisfactory results. Kaufmann and Adams (*J. Amer. Chem. Soc.* 1923, **45**, 3029) found that tetrahydrofurfuryl alcohol was the main product of the hydrogenation of furfural with Adams' catalyst in alcoholic solution; ferric chloride is a marked promoter for this reaction. Tetrahydrofurfuryl alcohol is now made on a large scale for use as a solvent

(U.S.P. 1703697). Wienhaus (*Ber.* 1913, **46**, 1927; 1920, **53** [B], 1656) has successfully hydrogenated furan rings with a colloidal palladium catalyst. Pyrones may be smoothly hydrogenated in the nucleus with colloidal palladium or with platinum black (Borsche *et al.*, *ibid.* 1915, **48**, 682; 1920, **59** [B], 237).

**Carbonyl Compounds.**—Hydrogenation of a carbonyl compound may yield either an alcohol or a hydrocarbon:



With platinum black, alcohol formation occurs readily with aromatic aldehydes and with cyclic ketones; in other cases the reaction is generally slower. In those cases in which much hydrocarbon tends to be formed (e.g. citral, acetone, acetoacetic ester, acetophenone) the use of aqueous alcohol as solvent diminishes the yield of hydrocarbon (Vavon, *Compt. rend.* 1911, **153**, 68; *Ann. Chim.* 1914, [ix], **1**, 148; Shriner and Adams, *J. Amer. Chem. Soc.* 1924, **46**, 1683). Failla (Ann. Chim. 1925, [x], **4**, 156) observed that the presence of traces of iron or aluminium in the platinum catalyst favoured alcohol formation, a promoter action with these metals was observed by Shriner and Adams (*J. Amer. Chem. Soc.* 1923, **45**, 2171) and by Carothers and Adams (*ibid.* 1925, **47**, 1047). Sabatier and Senderens (*Compt. rend.* 1903, **137**, 301; *cf.* Amouroux, *Bull. Soc. chim.* 1910, [iv], **7**, 154) found that aliphatic aldehydes and ketones were satisfactorily hydrogenated to alcohols in the vapour-phase over nickel; cyclopentanones generally gave considerable amounts of by-product (*cf.* Zelinsky, *Ber.* 1911, **44**, 2779, 2781, 2782; Godchot and Taboury, *Compt. rend.* 1911, **152**, 881; 1913, **156**, 470; *Bull. Soc. chim.* 1913, [iv], **13**, 591) but cyclohexanones were reduced normally (Sabatier and Senderens, *Ann. Chim. Phys.* 1905, [viii], **4**, 402; Haller and Martine, *Compt. rend.* 1905, **140**, 1298). Using nickel under pressure, Ipatiev (*Ber.* 1907, **40**, 1270) found that an equilibrium:



was set up, the same mixture of alcohol and ketone being obtained from either pure component. J. von Braun and Kochendörfer (*ibid.* 1923, **56** [B], 2172), however, applied the Schroeter procedure to a number of carbonyl compounds and achieved smooth formation of alcohols, except with aliphatic aldehydes, which yielded varying amounts of bimolecular *sec.* alcohol (*cf.* Von Braun and Manz, *ibid.* 1934, **67** [B], 1696). Both Raney nickel and copper chromite are good catalysts for the hydrogenation of ketones to alcohols by the Adkins method (Adkins and Cramer, *J. Amer. Chem. Soc.* 1930, **52**, 4349; Adkins and Connor, *ibid.* 1931, **53**, 1091; Covert and Adkins, *ibid.* 1932, **54**, 4116; Zartman and Adkins, *ibid.* 1932, **54**, 1668). Delépine and Horeau (*Compt. rend.* 1935, **201**, 1301; 1936, **202**, 995; *Bull. Soc. chim.* 1937, [v], **4**, 31) find that the hydrogenation of carbonyl compounds with Raney nickel is

petroleum before weighing. Among the arsenicals which gave good results by this method were "Stovarsol" and cacodylic acid.<sup>57</sup>

**Mercury.**<sup>57</sup>—The apparatus is very similar to that used for arsenic, except that a weighed U-tube cooled in a water bath acts as the receiver. If the substance contains any halogen element it is mixed with sodium sulphide, and the boat is enclosed in a cylinder of filter paper to protect the quartz tube.

**Cadmium.**<sup>58</sup>—The substance is mixed with calcium carbonate if sulphur or halogens are present, and the cadmium is distilled over into a weighed tube.

**Zinc.**<sup>58</sup> compounds when treated in the same way yield a deposit of metal mixed with oxide, which is dissolved in nitric acid, the solution evaporated and the residue ignited and weighed.

*Note.*—The asbestos layer, which acts as a decomposition catalyst, is heated by a Fletcher gas furnace, or electrically. Ter Meulen and Lacourt however recommend for this purpose Van den Berg's furnace simply constructed by boring a diatomite brick with holes for the tube and for three Bunsen burners.<sup>6, 28, 27</sup>

**Estimation of Sulphur.**<sup>1, 4, 6</sup>—A quartz tube 40 cm. long contains a boat holding 20–50 mg. of the sample followed by a 20 cm. layer, of platinised asbestos.<sup>1, 3, 4, 6</sup> The air in the tube is displaced by CO<sub>2</sub> before admitting a current of hydrogen which has passed through acid permanganate, alkaline permanganate and silver sulphate solutions but need not be dried. Substances which char considerably must be mixed in the boat with 0.5 g. platinum black.<sup>60</sup> The absorbent for the H<sub>2</sub>S evolved is a 10% solution of zinc sulphate to which an equal volume of 10% sodium acetate and a drop of acetic acid have been added. This is contained in a U-tube with one wide arm. The analysis is finished by adding an excess of standard iodine and a few c.c. of dilute HCl to the cool absorbent and titrating with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (Vol. II, 666). Gauthier<sup>8</sup> used platinised pumice in a hard glass tube for his accurate analyses of sulphonal, thiourea, etc. Alkali sulphonates were heated as usual, allowed to cool, a little HCl added to the residue in the boat and the process repeated. Similarly a second heating with addition of 10 mg. borax was necessary for metallic organic compounds (20 mg. taken) and for coal (50 mg.). Sulphates are mixed with H<sub>3</sub>BO<sub>3</sub> before reduction.<sup>61</sup> For difficult substances, e.g. thianthrene, ter Meulen<sup>6, 9</sup> replaced the usual catalyst by two separate spirals of platinum foil; see also Lacourt.<sup>7</sup> In Gel'man's *micro method for sulphur*<sup>11</sup> the vapours from 3–5 mg. of the substance pass with the hydrogen over Pt gauze; cf. Lacourt.<sup>10</sup>

Nickel catalysts absorb S and can not be used here. Pure asbestos at a high temperature, instead of Pt-asbestos or Pt-pumice, has been tried.<sup>52</sup> The substance may be heated by an Al block, bored to hold the tube, while the catalyst is conveniently heated in Van den Berg's furnace. Small quantities of sulphur are estimated colorimetrically.<sup>3</sup>

**Estimation of Halogens.**<sup>29</sup>—A current of hydrogen saturated with ammonia is passed

over 50 mg. of the sample which is cautiously heated in an otherwise empty quartz tube heated to redness beyond the boat. A sublimate of ammonium halide forms in the 40 cm. cold part of the tube.<sup>30</sup> When decomposition of the substance is complete (ca. 50 min.) the tube is washed out with water, the solution acidified with acetic acid, boiled for a few minutes (to expel any H<sub>2</sub>S or HCN present) and the halogen finally estimated gravimetrically (Br, I) or volumetrically (Cl).<sup>4, 7</sup> In an improved method<sup>13, 55</sup> the gases pass through a spiral of nickel foil or wire and finally over a boat containing BaCO<sub>3</sub>, both spiral and boat are heated to redness. The intermediate length of the tube is not heated. Halogen as barium and ammonium salt is estimated as usual. Results differed from those calculated by the following amounts: hexachloroethane, -0.4% Cl; dibromoanthracene, +0.1% Br; iodoform, -0.2% I. Gauthier<sup>8</sup> and Lacourt<sup>7</sup> were equally successful.

The *micro method for halogens* worked out by Lacourt<sup>10, 27</sup> depends on the properties of a nickel chromite catalyst<sup>32, 33, 36</sup> after prolonged treatment with aqueous and gaseous HCl until free from oxide. The substance, 2–5 mg., is heated in a current of pure H<sub>2</sub>, the vapours pass over 2 boats of the catalyst, for cracking and for hydrogenation at 450° respectively. The hydrogen halide formed is titrated after being absorbed in water in a U-tube (*v. Sulphur*) kept just alkaline to Methyl Red by additions of 0.02N-alkali from a microburette.<sup>23</sup> Among the results were: carbon tetrachloride, 2.163 mg., found 92.25% Cl (92.22), time 5 minutes. Pentabromotoluene, 2.751 mg., found 84.62% Br (84.55), 16 minutes. Iodocamphor, 4.952 mg., found 45.67% I (45.65), 12 minutes. A new tube is in condition when the escaping hydrogen has no effect on the indicator.<sup>27</sup>

**Estimation of Nitrogen.**<sup>3, 4, 12</sup>—The substance, 10 mg.,<sup>7, 10</sup> is mixed with 0.1 g. activated nickel<sup>14</sup> and heated by an Al block,<sup>6</sup> 9 × 4 × 4 cm., bored to hold the hard glass tube; another block, 12 × 4 × 4 cm., serves to heat the catalyst (Ni + 10% ThO<sub>2</sub> on asbestos) to 350°, or to 250° for hydrazides. A current of purified hydrogen (*v. "Estimation of Sulphur," supra*) carries the NH<sub>3</sub> formed through a little water contained in the U-tube already described. This water is kept faintly acid to Methyl Orange by adding 0.1N-HCl from a microburette<sup>23</sup> (fig. 3).

Weygand<sup>19</sup> recommends asbestos cardboard ovens<sup>3</sup> for heating the tube, nickel reduced from the formate in the tube and 0.05N-HCl for titrating. A cork connection is avoided by drawing out and bending the outlet end of the tube. If the sample contains S, Cl, Br or I, 2 cm. of soda-lime is placed before the catalyst.<sup>14, 20</sup> The preparation of the activated catalyst has been described already (p. 360c). Several workers have compared Kjeldahl's method with ter Meulen's, the latter being preferable except when a large number of analyses must be made daily.<sup>14, 15, 21, 25, 31</sup>

Heertjes<sup>22</sup> analysed 10 mg. samples of trinitro aromatic bodies by mixing 10 mg. with 1 g. of activated Ni in the boat, improving contact by adding a few drops of acetone. Similarly

dilute KOH is added to a mixture of protein and catalyst.<sup>6, 14</sup> The accuracy of the method is about  $\pm 0.2\%$ . Gauthier<sup>6</sup> found 14.66% N in antipyrine (calc. 14.89). Activated nickel is essential for difficult substances such as semicarbazides.

The progress of the analysis is followed and regulated by means of ter Meulen's method of continued titration. When ammonia ceases to be evolved, the boat is heated by the full flame

of the burner until decomposition has ceased. Owing to the small volume of absorbent water in the U-tube, 0.015 c.c. of 0.01N-acid causes a change in the indicator, corresponding to about 0.002 mg. N. An analysis requires about 10 minutes. Nickel formate,<sup>19, 38</sup> oxalate<sup>45</sup> and oxide usually contain nitrogen; they are reduced in the tube while a titration is carried out as for an analysis until all the nitrogen has been expelled.

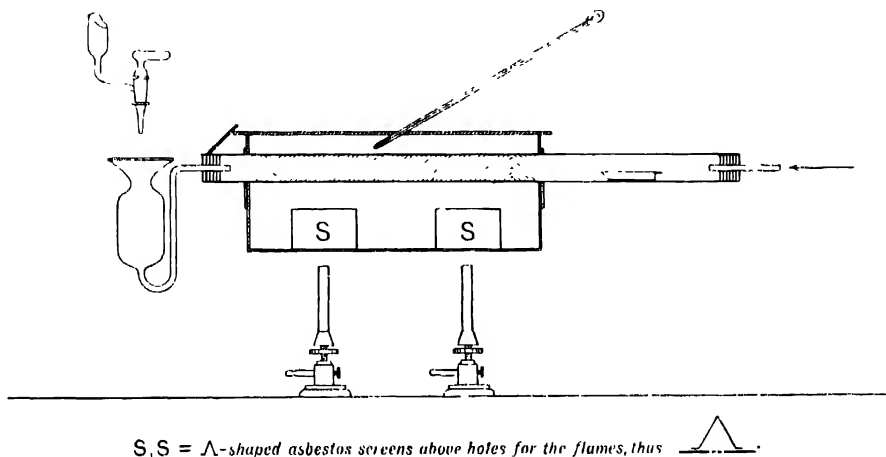


FIG. 3.—ESTIMATION OF NITROGEN.

The references may be classified mainly according to the elements determined:

*Oxygen, gravimetric*, 2, 3, 4, 10, 27, 32, 33, 34, 35, 36, 38, 39, 45, 46. *Oxygen, volumetric*, 27, 37, 40, 41.

*Nitrogen, volumetric*, 3, 10, 12, 14, 15, 19, 20, 21, 22, 24, 25, 31.

*Sulphur, volumetric*, 1, 3, 4, 6, 7, 8, 10, 11, 52.

*Halogens, volumetric and gravimetric*, 3, 13, 14, 29, 30, 55. *Halogens, by direct titration*, 27.

*Arsenic*, 3, 4, 7, 57. *Mercury*, 3, 4, 7, 57. *Cadmium*, 7, 58. *Zinc*, 58.

*Reviews of the methods*, 3, 4, 6, 7, 8, 9, 10, 65. *Monographs*, 3, 5. *Textbook article on nitrogen*, 19. *Nickel catalyst*, 2, 3, 4, 14, 19. *Nickel-thoria catalyst*, 6, 7, 32, 33, 34, 37, 38. *Nickel chromite catalyst*, 27, 28, 35, 40, 41. *Absorption tubes and Flow meters*, 16, 17, 18, 19, 23, 48, 49, 62, 63. *Furnaces*, 3, 4, 6, 19, 26, 32, 62. *Cinnamoyl chloride*, 27, 40, 41, 51.  *$\alpha$ -Naphthylory-chlorophosphine*, 37, 47. *Errors*, 34, 42, 43, 44. *Comparison with Kjeldahl's method*, 14, 21, 25. *Microtitrations*, 64.

1. H. ter Meulen, *Rec. trav. chim.* 1922, **41**, 112.

2. H. ter Meulen, *Rec. trav. chim.* 1922, **41**, 509; 1924, **43**, 899.

3. H. ter Meulen and J. Heshinga in J. F. Thorpe and M. A. Whiteley, "A Student's Manual of Organic Chemical Analysis," Longmans, London, 1926, pp. 254-277, 279-282.

4. H. ter Meulen, *Bull. Soc. chim.* 1931, [iv], **49**, i, 1098.

5. H. ter Meulen and J. Heshinga, "Nouvelles Méthodes d'Analyses Chimiques Organiques," Dunod, Paris, 1932.

6. H. ter Meulen, *Rec. trav. chim.* 1934, **53**, 118.

7. A. Lacourt, *Bull. Soc. chim. Belg.* 1934, **43**, 92, 93.

8. J. Gauthier, *Bull. Soc. chim.* 1935, [v], **2**, 322.

9. H. ter Meulen, *Bull. Soc. chim.* 1935, [v], **2**, 1692.

10. A. Lacourt, *Compt. rend.* 1936, **203**, 1367.

11. N. E. Gel'man, *Amer. Chem. Abstr.* 1940, **34**, 52.

12. H. ter Meulen, *Rec. trav. chim.* 1924, **43**, 643.

13. H. ter Meulen, *Rec. trav. chim.* 1928, **47**, 698.

14. H. ter Meulen, *Rec. trav. chim.* 1930, **49**, 396.

15. E. P. Griffing and C. L. Alsberg, *J. Amer. Chem. Soc.* 1931, **53**, 1037.

16. A. Friedrich, *Mikrochem.* 1935, **19**, 23.

17. R. Belcher and F. Smith, *Fuel*, 1940, **19**, 183.

18. A. Friedrich, *Mikrochem.* 1932, **10**, 329.

19. C. Weygand, "Organisch-chemische Experimentientekunst," Leipzig, 1938, p. 616.

20. H. ter Meulen and H. J. Ravenswaay, *Chem. Weekblad*, 1936, **33**, 248.

21. H. ter Meulen and K. Peeren, *J. Inst. Brew.* 1932, **38**, 330.
22. P. M. Heertjes, *Chem. Weekblad*, 1937, **34**, 827.
23. H. Briscoe and J. Matthews, "Microchemical Methods," Institute of Chemistry Lecture, 1934.
24. H. ter Meulen and H. J. Ravenswaay, *Rec. trav. chim.* 1937, **56**, 1022.
25. F. L. Smith and A. P. West, *Philippine J. Sci.* 1926, **31**, 265.
26. J. van den Berg, *Chem. Weekblad*, 1934, **31**, 24.
27. A. Lacourt, *Mikrochem.* 1938, **23**, 308.
28. J. C. Frazer and C. B. Jackson, *J. Amer. Chem. Soc.* 1936, **58**, 950.
29. H. ter Meulen and J. Heslinga, *Rec. trav. chim.* 1923, **42**, 1093.
30. M. Cohen, *Chem. Weekblad*, 1926, **23**, 232.
31. H. ter Meulen, *Rec. trav. chim.* 1927, **46**, 284.
32. W. W. Russell and J. W. Fulton, *Ind. Eng. Chem. [Anal.]*, 1933, **5**, 384.
33. W. W. Russell and M. E. Marks, *Ind. Eng. Chem. [Anal.]*, 1934, **6**, 381; 1936, **8**, 453.
34. W. R. Kirner, *Ind. Eng. Chem. [Anal.]*, 1937, **9**, 535.
35. P. Goodloe and J. C. Frazer, *Ind. Eng. Chem. [Anal.]*, 1937, **9**, 223.
36. M. E. Marks, *Ind. Eng. Chem. [Anal.]*, 1935, **7**, 102.
37. J. Lindner and W. Wirth, *Ber.* 1937, **70** [B], 1025.
38. J. Unterzaucher and K. Bürger, *Ber.* 1938, **71** [B], 429.
39. H. ter Meulen, H. J. Ravenswaay and J. de Veer, *Chem. Weekblad*, 1930, **27**, 18.
40. A. Lacourt, *Compt. rend.* 1937, **205**, 280.
41. A. Lacourt, *Bull. Soc. chim. Belg.* 1937, **46**, 428.
42. Hans Meyer, "Analyse und Konstitutions-Ermittlung organischer Verbindungen," 6th ed., 1938, pp. 112, 252.
43. J. Lindner, *Ber.* 1934, **67** [B], 1652.
44. J. Lindner, "Mikro-massanalytische Bestimmung des Kohlenstoffes und Wasserstoffes," Berlin, 1935.
45. H. Hennig, *Chem. Fabrik*, 1936, **9**, 239.
46. C. Weygand and H. Hennig, *Chem. Fabrik*, 1936, **9**, 8.
47. J. Lindner, *Chem. Ztg.* 1931, **55**, 308.
48. F. Pregl, "Quantitative organische Mikroanalyse," 3rd ed., 1930.
49. B. Flaschenträger, *Z. angew. Chem.* 1926, **39**, 720.
50. E. Muller and H. Willenberg, *J. pr. Chem.* 1919, [ii], **99**, 34.
51. C. van Nieuwenburg, *Mikrochim. Acta*, 1937, **1**, 71.
52. H. ter Meulen, H. F. Opwyrd and H. J. Ravenswaay, *Chem. Weekblad*, 1930, **27**, 19.
53. H. ter Meulen, *Chem. Weekblad*, 1926, **23**, 348.
54. M. Schütze, *Z. anal. Chem.* 1939, **118**, 245.
55. W. Theilacker and E. Gessner, *Angew. Chem.* 1938, **51**, 892.
56. W. Zimmermann, *Z. anal. Chem.* 1939, **118**, 258.
57. H. ter Meulen, *Rec. trav. chim.* 1926, **45**, 365, 368.
58. H. ter Meulen and H. J. Ravenswaay, *Rec. trav. chim.* 1929, **48**, 198.
59. R. Belcher, *Chem. and Ind.* 1941, **60**, 608.
60. L. Pigeon, *Ann. Chim. Phys.* 1894, [vii], **2**, 451.
61. H. ter Meulen, *Chem. Zentr.* 1927, **i**, 325.
62. L. T. Hallett and G. Kemmerer, *Ind. Eng. Chem.* 1927, **19**, 173.
63. A. Friedrich, "Praxis der quantitativen organischen Mikroanalyse," 1933, p. 23.
64. J. B. Niederl, V. Niederl and M. Eitingon, *Mikrochem.* 1938, **25**, 143.
65. J. G. A. Griffiths *et al.*, *Chem. Soc. Annual Rep.* 1938, **35**, 408.

J. N. G.

**HYDROGENATION OF COAL.**

Coal, compared with oil, is deficient in disposable hydrogen, that is, hydrogen surplus to that required for combination with oxygen, nitrogen and sulphur. It follows that one essential of a complete transformation of bituminous coal to petrol, if such were possible, is to increase the hydrogen content by about 170%, or in the case of lignite, by 140%. These figures must, of course, be modified considerably in either direction with the different varieties of bituminous coals and lignites.

**Historical Survey.**—The original conception of the hydrogenation of coal to give oil was due to Dr. Friedrich Bergius. His experiments started before the war (1914–18) and ended with a small semi-technical plant at Rheinau, near Mannheim, which was in operation until 1927. After the war, the I.G. Farbenindustrie started work independently and brought to bear on the problem their knowledge of high pressure technique and of catalysts. They made two important advances—the discovery of catalysts immune to sulphur poisoning and the division of the hydrogenation process into liquid and vapour phase stages.

Developments in Germany then passed wholly into their hands and they built the first commercial hydrogenation plant at Leuna in 1927. This was designed to produce 100,000 tons per year of petrol from brown coal, but at first it was operated mostly on low-temperature tar made from brown coal and on German crude petroleum. Experimental work was also done with bituminous coal. The applicability of the process to the petroleum industry was soon recognised and a joint company for its exploitation was formed by the I.G. and the Standard Oil Co. (New Jersey).

Meanwhile the original Bergius process had been considered for British conditions, and tests on British coals were made at Rheinau. Research work was inaugurated at the Fuel Research Station of the Department of Scientific and Industrial Research in 1922, and in 1926 an intermediate-scale continuous plant, on the lines of the latest Bergius development, was set up. An agreement was entered into between the British Government and Dr. Bergius for the pooling and mutual discussion of the results obtained in both laboratories, and an option on the patent rights for the British Empire was secured by the British Bergius Syndicate from the International Bergin Company.

In 1927 Imperial Chemical Industries acquired the British Bergius Syndicate and started independent research on the process. It was decided that the original Bergius method of operation to give a variety of products—petrol, tar acids, heavy oil and pitch, was not profitable, but that it would be attractive if it could be modified to produce petrol as the only liquid product.

In 1929 I.C.I. built at Billingham a pilot plant to treat 10 tons of coal per day, and this plant was run until the end of 1931. None of the practical difficulties which arose were found to be insuperable, and in 1930 I.C.I. announced that they could produce a 60% weight yield of petrol from coal, and gave estimated costs which showed that commercial development was possible only with Government assistance.

As the process developed it was realised that many important patents in the hydrogenation field were held by the Standard-I.G. group. Discussions were opened, as a result of which the four major operators in the field—the I.G. of Germany, the Standard Oil Co. (New Jersey), the Royal-Dutch-Shell Group and I.C.I.—associated themselves through a pooling company, The International Hydrogenation Patents Company (I.H.P.), in order to pool their patent rights and to effect a general exchange of technical information.

In 1931 the I.G. resumed the hydrogenation of brown coal on a large scale and this now provides a large part of the output of the hydrogenation plants in Germany. Meanwhile, I.C.I. concentrated their research on the treatment of bituminous coal, and by the end of 1932 had prepared schemes for building a large hydrogenation plant at Billingham, which was put in hand in July, 1933, when the Government announced their intention to guarantee the continuance of the preference on light oils made from indigenous materials for a period of years.

The plant, with a production capacity of 150,000 tons per year of petrol, was started up early in 1935, and has been in continuous operation hydrogenating coal and creosote oil up to the present time.

Pursuing her policy of home production of essential materials, Germany has, subsequent to the erection of the Billingham plant, constructed a number of bituminous coal hydrogenation units of similar size.

**General Theoretical Considerations.**—All hydrogenation processes consist essentially in subjecting coal to the action of hydrogen at a high temperature and a high pressure.

Three types of reaction are involved. The first is the transformation of impure carbonaceous material to a product of substantially hydrocarbon composition, elements other than carbon and hydrogen being removed by combination with hydrogen. Oxygen thus forms water, nitrogen forms ammonia and sulphur forms hydrogen sulphide.

The second type is the splitting of the "hydrocarbon" molecules to saturated and unsaturated hydrocarbons of lower molecular weight.

The third reaction consists of the saturation of the unsaturated hydrocarbons immediately they are formed.

For satisfactory control of the hydrogenation process it is essential that the second reaction should not be allowed to outpace reactions one and three. Otherwise, splitting to hydrocarbon gas and polymerisation of intermediate unsaturated products to coke takes place, with consequent loss in yield of liquid hydrocarbons.

Because the required severity of splitting conditions increases as the size of molecule to be split is decreased, this balancing of the reactions is assisted by dividing the process into stages. In the first stage the conditions may be such that the reduction reaction takes place with maximum efficiency, accompanied by relatively little splitting. This gives rise mainly to a heavy oil product, the approximate composition of which is shown in fig. 1. In the second stage rather more severe splitting conditions are employed, and heavy oil is broken down to give as the main product a middle oil of final boiling-point of the order of 320°C. This middle oil is sufficiently volatile for it to be fairly easily vaporised under the temperature

BITUMINOUS COAL	CARBON	$\frac{H_2}{N_2}$ $\frac{H_2}{NH_3}$	
		H <sub>2</sub>	NH <sub>3</sub>
	94	6	11
PRIMA-RY HEAVY OIL			
	92	8	5
MIDDLE OIL			
	90	10	4
PETROLS—Composition depending on V.P. Catalyst used			
	88	12	
	85	15	

FIG. 1.

conditions required for the final stage of splitting to petrol. This enables the reaction to be carried out entirely in the vapour phase and in the presence of a high concentration of active solid catalyst.

In practice, subdivision of the process into two stages—*liquid phase* hydrogenation of coal to middle oil and *vapour phase* treatment of middle oil over solid catalyst—has been found to be essential for production of good quality petrol in economic yield. The use of two liquid phase stages, although advantageous, is probably not worth the additional complications, except in very large plant.

#### LIQUID PHASE COAL HYDROGENATION.

(a) *Plant.*—The preliminary Bergius experiments were carried out in two-litre steel autoclaves arranged to rotate over a row of gas burners. The autoclaves were fitted with a pressure gauge and a thermo-couple pocket.

This type of apparatus utilises the batch principle. Coal or coal paste is placed in the autoclave, which is closed and hydrogen admitted to a pressure of about 100 atm. The

converter is then heated to a temperature of approximately  $450^{\circ}\text{C}.$ , the pressure rising to about 250 atm., and is maintained at this temperature for about two hours. The apparatus is then cooled, and the gas let down to a holder for analysis. The liquid product remaining in the autoclave is subjected to analysis to determine the extent of conversion of the coal and the character of the oil product.

The apparatus has been studiously copied by later investigators in order to study the chemistry of the reaction and the effect of catalysts.

The larger continuous type of apparatus used by Bergius and later by the Fuel Research Station is shown in fig. 2. Coal made into a paste with recycle oil from the hydrogenation reaction is forced into the converter system by pump (A). From the pump the paste, which is kept agitated by mechanical stirrers, passes successively through three converters, C, D and E, which are surrounded by baths of molten

lead, hydrogen of about 90% purity at the same time being pumped in at 200 atm. pressure by means of a four-stage compressor B. In this arrangement the first converter is used mainly as a heating chamber, being brought to a temperature just short of that necessary for the hydrogenation reaction at 200 atm. The second and third converters are maintained at the temperature which previous experiments have shown to give the best results for the particular type of coal under treatment. On completing its course through the converters, which takes about two hours, the hydrogenated product and surplus hydrogen are cooled in the condensers F and are then passed through a reducing valve G which lowers their pressure to 60 atm. They are then allowed to separate in the separator H. From H the gas is taken to a scrubber I, where, still at a pressure of 60 atm., it is scrubbed with oil for recovery of the light spirit. At intervals of approximately an hour the liquids remaining in the separator H are

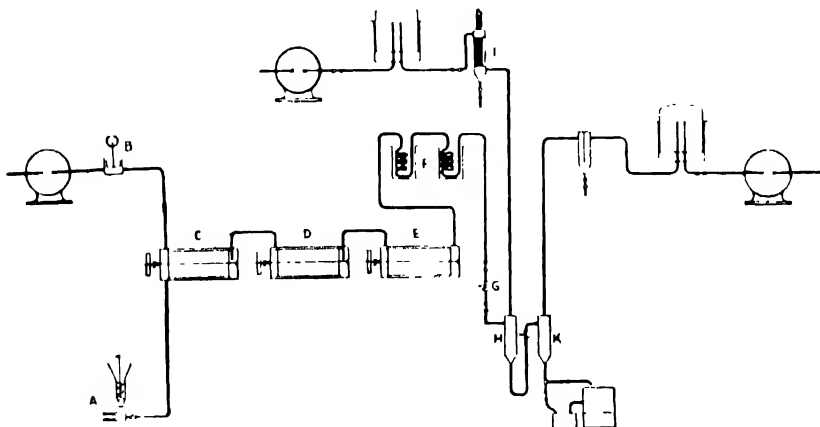


FIG. 2.-BERGIUS HYDROGENATION PLANT. MEDIUM SCALE, CONTINUOUS PROCESS. ONE TON COAL PER DAY.

blown down to the atmospheric separator K, when further gas is given off which is passed to the gasholder. The liquid product, which consists of a mobile oil, is periodically run off to storage tanks, either directly or after centrifuging.

By 1938 both the I.G. and I.C.I. had independently shown that the process could be more conveniently carried out using a relatively thin coal paste (50% coal) hydrogenated in a simple vertical reaction vessel. Because of the exothermic nature of the reaction, it is unnecessary to heat the converters externally except in the case of very small experimental plant, and the passage of the hydrogen bubbles through the reacting liquid provides sufficient stirring action to dispense with the use of mechanical stirrers.

The arrangement of a small semi-technical plant based on this principle is shown in fig. 3. Coal paste is injected by means of one of two hand-operated accumulators. This consists of a steam jacketed steel cylinder in which is fitted a piston. Coal paste is introduced on the

upper side of the piston by means of medium gas pressure. The filling line is then closed and the paste forced from the accumulator by application of 300 atm. water or gas to the under side of the piston. From the accumulator the paste passes to a preheater coil immersed in a lead bath and, just before entering the preheater, is joined by a stream of high-pressure hydrogen. From the preheater the mixed reactants pass, at a temperature of approximately  $420^{\circ}\text{C}.$ , to a converter consisting of a vertical chrome steel tube 26' high and 4" internal diameter. Excessive heat loss from the converter is guarded against by a series of electric windings. The products from the top of the converter pass to a high-pressure vessel maintained at about  $450^{\circ}\text{C}.$ , where products which are liquid under reaction conditions are separated from those which are vaporised. The liquid contents of the hot separator are let down periodically to atmospheric pressure and the gas and vapours pass through a cooler to a cold high-pressure separator, which is again let down

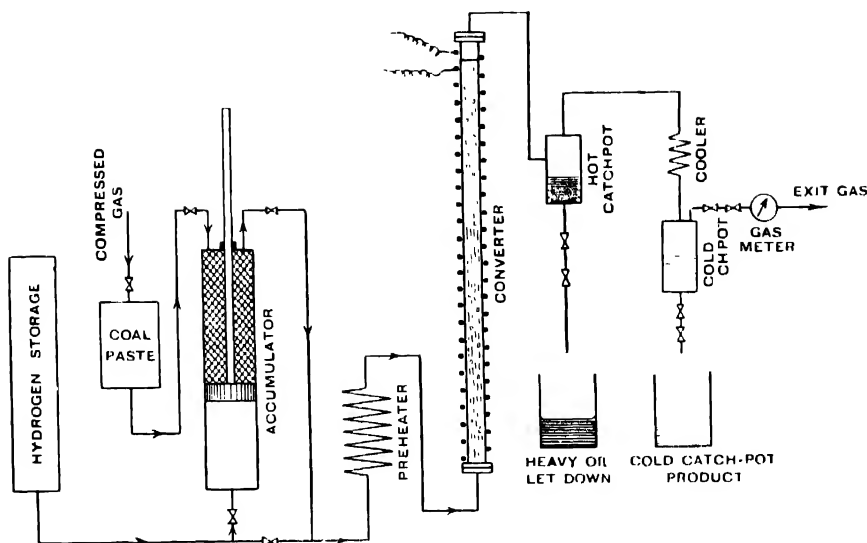


FIG. 3.

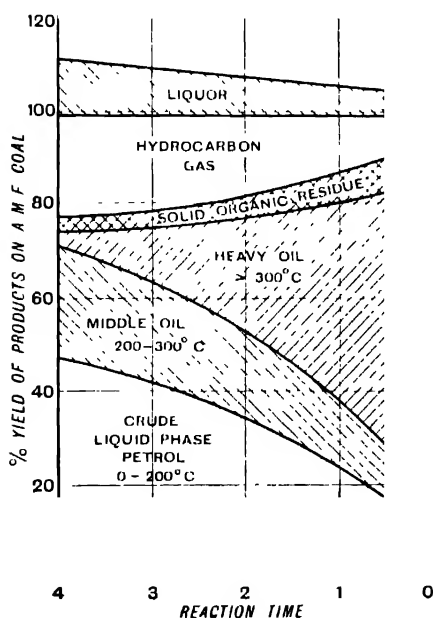


FIG. 4.

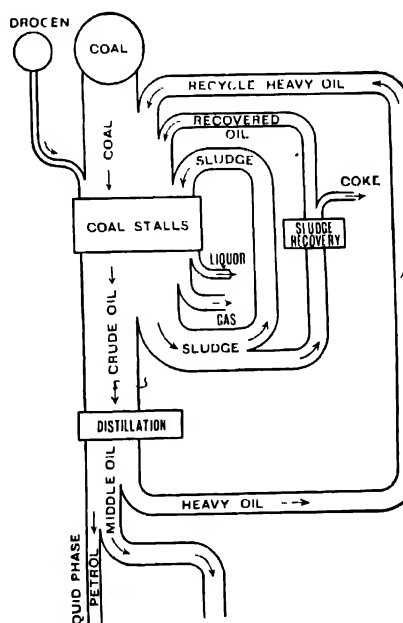


FIG. 5.

periodically. Exit gas is let down to atmospheric pressure, and measured with an ordinary rotary meter.

The heavy oil let down from the hot separator is centrifuged in order to remove ash and unconverted coal, and the filtrate is recycled as pasting oil. The cold catch-pot product is allowed to stand and liquor separated off. It is then fractionated into petrol, middle oil and heavy oil. Part or the whole of the heavy oil

is recycled, depending on whether a single or two-stage liquid phase process is being employed. The proportion of heavy oil in the newly formed products can be varied by control of temperature or reaction time in the converters. This control is illustrated by fig. 4, which shows the effect of reaction time on the products of coal hydrogenation. The method of operation with single stage and with 2-stage liquid-phase hydrogenation is shown in figs. 5 and 6.

The large scale adaptation of the vertical converter principle is shown in Fig. 7. Operation is the same as in the case of the semi-technical unit, except that the converters have to be cooled by the injection of cold hydrogen, and that heat exchangers are fitted before the preheater by means of which the ingoing feed is heated by the exit product from the converter.

(b) Catalysts.—No catalyst was employed in the original Bergius experiments. Later it was found advantageous to use a small quantity of *lurmanse*.

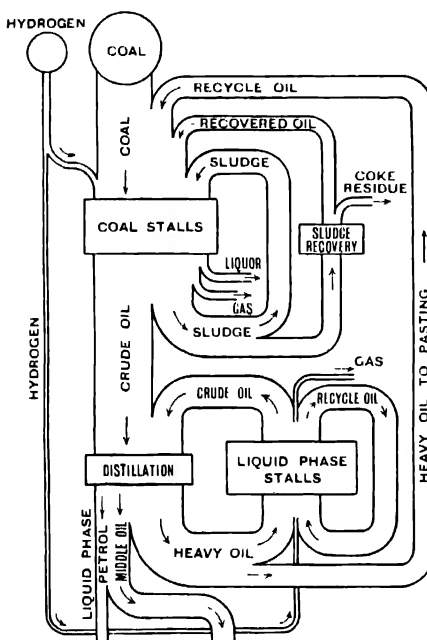


Fig. 6.

In 1929 I.C.I. found that tin was the most promising catalyst for bituminous-coal liquefaction. It was first used in the form of grids of tinned iron fixed inside the converters. Later, continuous injection with the coal paste of a very small amount of certain organic compounds of tin was found to be preferable.

This superiority of tin compounds as catalyst for coal liquefaction was also demonstrated by experiments carried out by the Fuel Research Board and published in the Annual Report for 1932 (see Table I).

Alkalis have a deleterious effect on the coal liquefaction reaction. A large proportion of the alkaline constituents of coal can be removed by efficient coal cleaning, which, in any case, is obviously beneficial in that it decreases the amount of material which has to be purged from the process by centrifuging.

Hydrogen chloride can advantageously be added to the reaction in order to neutralise any remaining alkali. This introduces corrosion problems on the exit side of the converter system, but in 1933 a process was discovered

and patented by I.C.I. for the scrubbing of the exit vapours from the converter with a suspension of alkali in oil at a temperature of about 450°C. This reduces corrosion to a negligible amount.

(c) Quality of Product (from Bituminous Coal).—The petrol fraction obtained by distillation of the crude cold catch-pot product of liquid phase hydrogenation of coal or heavy oil can easily be refined by normal petroleum refinery methods. Refined petrol cut to a

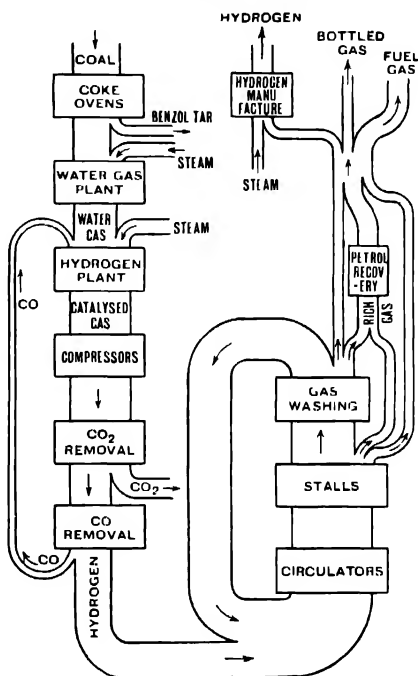


Fig. 7.

volatility of 40% at 100°C. has the following properties:

Specific gravity at 15°	0.740-0.745
Initial b.p.	35°C.
90% vol. recovered at	158°C.
Final b.p.	170°C.
Residue	1.0%
Loss	1.0%
% distillation+loss at 70°C.	20%
" " " 100°C.	40%
" " " 140°C.	75%
Roid vapour pressure at 100°F.	9 lbs./sq. in.
Octane No. C.F.R. motor method	71-73
" " C.F.R. aviation method	—
Colour	+25 Saybolt
Odour	Marketable
Sulphur, % by weight	0.05
Doctor test	Negative
A.S.T.M. copper strip corrosion test	Negative
Gum, Pyrex dish without air jet (mg./100 mls.)	2.0



TABLE I.—EFFECT OF CATALYSTS ON THE HYDROGENATION OF COAL.

Catalyst.	Percentage catalyst on coal charged.	Product per cent. of ash-free dry coal.			
		Insoluble in chloroform.	Soluble in chloroform.	Water.	Gas.
—	2.5	49.2	27.6	7.1	10.7
Luxmasse	2.5	10.0	66.1	5.9	8.2
ZnO . . .	2.5	10.2	70.4	5.6	7.6
SnO <sub>2</sub> . . .	2.5	7.7	71.2	7.7	6.2
MoO <sub>3</sub> . . .	2.5	14.1	59.2	7.6	9.3
Fe <sub>2</sub> O <sub>3</sub> . . .	2.5	27.3	52.4	2.0	8.8
TiO <sub>2</sub> . . .	2.5	36.9	38.2	7.2	10.8
Fe <sub>2</sub> O <sub>3</sub> . . .	2.29	12.0	65.7	6.9	6.5
TiO <sub>2</sub> . . .	0.21				
FeC <sub>2</sub> O <sub>4</sub> . . .	2.5	18.0	56.8	6.2	9.4
V <sub>2</sub> O <sub>5</sub> . . .	2.5	49.8	24.7	6.6	10.2
Nickel oleate	2.5	10.2	67.6	6.3	8.7
Pb(OH) <sub>2</sub> . . .	0.1	12.2	65.4	7.0	8.8
CeO <sub>2</sub> . . .	0.1	10.5	62.3	7.9	11.3
SnS . . .	0.1	10.5	63.1	6.3	—
SnS <sub>2</sub> . . .	0.1	11.6	61.3	7.8	—
Sn(OH) <sub>2</sub> . . .	2.5	6.1	71.9	7.0	5.8
" . . .	0.5	6.0	70.6	7.9	6.4
" . . .	0.1	10.9	63.4	6.9	8.5
" . . .	0.01	10.6	64.2	7.1	6.2
" . . .	0.0027	15.1	58.8	7.2	8.5
" . . .	0.00067	38.3	36.5	7.0	16.5

The middle oil fraction, which usually has a distillation range of 170–320°C., contains about 8% of tar acids, the remainder consisting of about 95% of aromatic hydrocarbons. Without further treatment the ignition properties of this oil are not suitable for its use as a Diesel fuel. It may, however, be saturated to a naphthenic product by vapour phase treatment at low temperature over active catalyst. The product is a reasonably good Diesel oil.

The heavy oil obtained directly from coal is suitable for use as fuel oil without any further treatment.

The products of liquid phase bituminous coal hydrogenation being mainly aromatic, it is unlikely that satisfactory lubricating oil fractions could be obtained by direct extraction or fractionation.

#### LIQUID PHASE HYDROGENATION OF HEAVY OIL.

When the coal hydrogenation stage is operated under conditions which give heavy oil in excess of that required for recycle as pasting oil, the surplus heavy oil is hydrogenated in a separate plant which is practically identical with that used for coal hydrogenation.

Liquid product from the hot separator, instead of being cooled and let down to atmospheric pressure, is recycled hot and under pressure to the inlet of the preheater. A comparatively small continuous purge is made from the hot catch-pot to prevent undue accumulation of solids and heavy asphaltic material. In this way a high concentration of suspended catalyst can, if desired, be built up in the reaction vessel.

VOL. VI.—24

The above method for liquid phase heavy oil hydrogenation has been developed to a considerable extent by the I.G., particularly in connection with the hydrogenation of brown coal tar. Supported molybdenum compounds are frequently used as catalyst.

For the hydrogenation of heavy oils free from asphaltic constituents the method may be modified by the use of fixed catalyst such as is used for vapour phase hydrogenation.

Temperature and throughout conditions in the heavy oil hydrogenation are controlled so that middle oil rather than petrol is the main product. The middle oil is further processed in the vapour phase hydrogenation section.

#### VAPOUR PHASE HYDROGENATION OF MIDDLE OIL.

(a) Plant.—In general, the plant used for vapour phase hydrogenation is very similar to that used in the liquid phase stage. Middle oil is injected into the plant by means of a pump usually working at a pressure of about 250 atm. It is joined by compressed hydrogen and passes to a preheater where it is completely vaporised at a temperature of the order of 350–400°C. The mixed vapour and hydrogen passes to a converter, which is packed with solid catalyst pellets, and operates at a reaction temperature varying between 350° and 550°C., depending on the nature of the catalyst employed.

On the large scale the catalyst is arranged in beds, between which cold hydrogen can be admitted in order to give control of the highly

exothermic reaction. The vapour phase nature of the reaction allows the hot catch-pot to be dispensed with, and the outgoing products pass to a cooler after exchanging part of their heat with the ingoing reactants. After the cooler, condensed liquid product is collected in a high-pressure separator, which is let down periodically. The product, which usually contains about 60–70% of petrol, is distilled to give petrol and a residual middle oil fraction, which is recycled to the reaction.

Apart from a simple washing of product to remove hydrogen sulphide and ammonia, petrol from vapour phase operation requires no refining treatment.

(b) Catalysts.—A range of catalysts satisfactory for the vapour phase hydrogenation of middle oils is known. At one end of the range these catalysts have a relatively high splitting and poor saturation activity, and these give rise to petrols of high aromatic content. Such catalysts require a comparatively high reaction temperature (about 500°C.) and, as a result, gas-make tends to be fairly high. At the other end of the range are catalysts of very marked saturation activity, which operate at lower temperatures (about 400°C.) and give high yields of petrol of low aromatic content.

TABLE II.

Constituent.	Vapour phase petrol. (Percentage vol. total petrol.)		
	Group I	Group II	Group III.
Butane . . . . .	5	5	5
isoParaffins (mainly single branch) . . . . .	5	28	30
Aromatics . . . . .	43	3	7
Unsaturated hydrocarbons . . . . .	3	—	—
Naphthenes boiling above 110°C. . . . .	18	25	28
Straight chain paraffins . . . . .	11	14	4
Octane No. unleaded (C.F.R. motor method) . . . . .	80	68–69	75–76
Octane No. with 4 c.c. T.E.L./gallon (C.F.R. motor method) . . . . .	86	86–87	89–90

An important class of catalyst has recently been developed with splitting-saturation activity intermediate between the extremes cited above. These catalysts, in addition to aiding the usual splitting and saturation reactions, also encourage isomerisation of cyclohexanes to substituted cyclopentane derivatives and give rise to a high ratio of branched to straight chain paraffin isomers.

The yield of petrol obtainable from a substantially hydrocarbon middle oil varies between 80 and 92% by weight, depending on the catalyst employed.

For a more complete description of the control of the vapour phase hydrogenation of middle oils by suitable choice of catalyst, the reader is referred to papers by M. Pier of I.G. Farbenindustrie, *see* particularly *Trans. Faraday Soc.*, 1939, 85, 967.

(c) Quality of Products.—Table II gives the composition and properties of petrols cut to 40% volatility at 100°C. obtainable from coal middle oil by vapour phase hydrogenation over the three types of catalyst mentioned above.

It will be observed that petrol from catalysts of Groups II and III, particularly that from Group III catalyst, has a very good lead susceptibility and that its octane number when leaded with 4 c.c. per gallon of lead tetraethyl is well up to the 87 required by the Air Ministry specification for aviation fuel. Recycle oil, particularly from catalysts of Group II, is a highly saturated naphthenic product free from phenols and bases, and is a reasonably good Diesel fuel, having the following properties:

Sp. gr. 15/15 . . . . .	0.8360
Flash point . . . . .	178°F. (81.2°C.)
Inst. Pet. Tech.:	
Initial b.p.°C. . . . .	217.5
10% at . . . . .	222.5
30% at . . . . .	227.0
60% at . . . . .	236.0
90% at . . . . .	257.0
Final b.p.°C. . . . .	283.0
Total distillate . . . . .	98.5%
Residue . . . . .	1.5%
Ash . . . . .	0.002%
Asphalt . . . . .	nil
Setting point . . . . .	below –50°F.
Total acidity equivalent to 13.5 mg. KOH/100 g. oil.	
Inorganic alkalinity equivalent to 1.2 mg. H <sub>2</sub> SO <sub>4</sub> /100 g. oil.	
Viscosity:	
32°F. Admiralty viscometer . . . . .	5.0 secs.
70°F. Redwood No. 1 . . . . .	33.5 „
140°F. „ „ . . . . .	28.3 „
Carbon . . . . .	85.94%
Hydrogen . . . . .	13.46%
Sulphur . . . . .	0.08%
Calorific value . . . . .	10,897 g.-cal.
Moore spontaneous ignition temperature . . . . .	265°C.

The hydrocarbon gases produced in vapour phase hydrogenation of the middle oils are composed largely of butane and propane, which can be transported as liquids and used for lighting, heating or petrol substitutes (*v. Gas, BOTTLE, Vol. V, 480*).

#### HYDROGEN CIRCULATION AND PURGE OF NITROGEN AND HYDROCARBON GASES.

On the large scale, the exit gas from the cold high-pressure separators of the liquid and vapour phase hydrogenation stalls is recycled to the reaction by means of circulators. Circulating hydrogen becomes impure, partly through accumulation of nitrogen from the make-up

gas and partly through accumulation of methane, ethane, propane and butane formed in the process. Part of these gases is removed by solution in the products themselves and is recovered when the cold catch-pot products are let down to atmospheric pressure. Final control of the purity of the circulating gas is obtained by scrubbing it with oil at full process pressure in a separate plant specially designed for the purpose.

The cold separator product and the oil used for washing circulating gas is usually let down to atmospheric pressure in a number of stages. In this way the least soluble of the gases, such as nitrogen, ethane and methane, are concentrated in the purge obtained on letting down from 250 to say 50 atm. pressure, and can conveniently be used as gaseous fuel. As the pressure is further released, richer gas containing increasingly high concentrations of butane and propane is evolved.

These rich gases are scrubbed with oil for recovery of pentane and low boiling petrol constituents and are the source of pure butane and propane.

#### HYDROGEN MANUFACTURE.

Hydrogen for hydrogenation is made from coke by first converting it to water gas, which is then treated with steam over a catalyst for conversion of the CO to CO<sub>2</sub>. Alternatively H<sub>2</sub> can be made by catalytic reaction of steam with the by-product hydrocarbon gas from the hydrogenation process. This latter process was worked out originally by the I.G. and the Standard Oil Co., which latter firm produce thereby all the hydrogen required for their hydrogenation plant.

The make-up hydrogen for the Billingham hydrogenation plant is made by combination of the two processes, and the flow diagram of the hydrogen production and treatment of hydrogenation-plant gases at Billingham is shown in fig. 7.

**Efficiency of Process.**—The yield of petrol from bituminous coal calculated on an ash- and moisture-free basis is of the order of 60% by weight.

A more important figure is the overall coal consumption. In the case of a plant in which all the H<sub>2</sub> requirement is obtained from the by-product hydrocarbon gases using the methane-steam process, it is estimated that the overall consumption of raw coal would vary from 3.5–4 tons of coal per ton of petrol, the exact figure depending on the ash and moisture content of the coal and its suitability for the process. This corresponds to a thermal efficiency of 40%, which compares favourably with 25% for generation of electric power and 55% for gasification.

In a plant in which the hydrogen is made via coke and water gas, the overall raw coal consumption is approximately 5 tons per ton of petrol, the higher figure being due to the lower efficiency of coke ovens followed by water-gas generators compared with catalytic manufacture of hydrogen from hydrocarbon gases. This is partly compensated for from the financial

point of view by the tar, benzol and gas made as carbonisation by-products.

#### THE HYDROGENATION OF COAL TARS.

Considerable research into the possibility of single stage hydrogenation of crude tars to petrol and light oils has been carried out by the Fuel Research Station of the Department of Scientific and Industrial Research at Greenwich, where a large semi-technical plant has been operated.

Both liquid and vapour phase reactions occur in the same converter, which contains fixed solid catalyst particles. The chief catalysts investigated have been molybdenum supported on charcoal or alumina and pelleted molybdenum sulphide. The disadvantage of the process lies in the slow deterioration of catalyst caused by the presence in the feed of asphaltic and high boiling constituents. Certain of the catalysts can, however, be revived by periodic treatment with air, and the rate of deterioration can be reduced by employment of high pressures of the order of 400 atm. The deterioration is greatest with tars produced under high temperature carbonisation conditions, and is negligible when distilled tar oils of reasonably low end-point are used as feed.

It was concluded that, although the single stage process may be suitable for certain selected tars of low asphalt content, division of the process into separate liquid phase and vapour phase stages is necessary for treatment of tars in general. Since 1936, work at Greenwich has been concentrated on the liquid phase stage using fairly high concentrations of dispersed catalyst. Low temperature, vertical retort and cannel tars and also shale oil have been studied.

This work is fully described in the Annual Reports of the Fuel Research Board and in a number of publications by the Board's investigators.

Tar and tar oils are being hydrogenated on a large scale in both Germany and England, using processes controlled by the I.H.P. Group. The exact method of operation varies in different plants, but the process consists essentially of separation of the tar or tar oils into a middle oil fraction suitable for true vapour phase hydrogenation and a heavy residue which is treated under the liquid phase conditions described for the hydrogenation of heavy oil from coal.

Fig. 8 illustrates a satisfactory method for the simultaneous hydrogenation of coal, creosote oil and low temperature tar which has been employed by the I.C.I. at Billingham. In order that solid and heavy asphaltic constituents can be purged from the system along with similar material present in the products of coal hydrogenation, crude low temperature tar is fed to the process as coal-pasting oil. Creosote is distilled to give a middle oil, which is treated in the vapour phase section, and a heavy residue which joins the feed of coal heavy oil to the second liquid phase hydrogenation stage.

Petrol yields from tar and tar oils are stated to be 80–90% by weight, depending on the raw material used.

The quality of hydrogenation products from coal-tar and tar oils depends on the character of the oil and on the type of catalyst employed in the vapour phase hydrogenation step. Using highly aromatic oils, such as creosote and low temperature tar from bituminous coal, petrol obtained with a given vapour phase catalyst

8. "Fest angeordneter Katalysator bei der Druckhydrierung." Pier, Oel u. Kohle, Erdoel u. Teer, 1937, 13, 916-20.

9. "Einfluss von Rohstoff, Katalysator und Arbeitsweise auf Hydrierbenzine." Pier, Angew. Chem., 1938, 51, 603-608.

10. "Die Behandlung von Schieferöl durch Hydrierung." Pier, J. Inst. Petroleum Tech., 1938, 24, 692-705.

11. "On the Reactions of the Catalytic High Pressure Hydrogenation of Coal and Oil, and their Control." Pier, Trans. Faraday Soc., 1939, 35, 967.

R. H.

### HYDROGENATION MECHANISM.—

The addition of hydrogen to inorganic and especially organic substances is a process of considerable technical importance; leading examples are the transformation of liquid into solid fats, the production of ammonia and the Fischer-Tropsch synthesis of hydrocarbons. Although the addition of hydrogen may be effected in certain cases at high temperatures in the absence of a catalyst, or by means of hydrogen atoms produced photochemically, in general it is carried out through the agency of a catalyst. It is these catalytic reactions which will be discussed here.

### THEORIES OF CATALYSIS.

The first observation on the effect of metals in inducing the reaction of hydrogen appears to be that of H. Davy (Phil. Trans. 1817, 107, 77) who found that a heated platinum spiral placed in a mixture of coal gas and air continued to glow. Somewhat later, Erman (Abh. K. Preuss. Akad. Wiss., 1818-19, 368) showed that the combination of oxygen and hydrogen could be induced by platinum at as low a temperature as 50°C. Faraday discussed the mode of action of the catalyst and concluded that it was intimately connected with the forces exerted by the metal on the gases—a view which is still held. Many theories have been proposed to account for catalytic phenomena. One explanation is brought about simply by the increase in concentration caused by condensation on the surface. This explanation is inadequate, not only on account of the extremely high concentrations which would be required, but also because it fails to account for the highly specific nature of catalysts and their sensitivity to traces of poisons. Catalysis cannot be interpreted simply as the modification of an already existing reaction mechanism, but involves the provision by the catalyst of an entirely new path of reaction in which the energies required to effect the steps are less than those required for the uncatalysed reaction.

Another explanation which has been put forward is the intermediate-compound theory. According to this, reaction takes place through the formation of a compound between one reactant and the catalyst; the other reactant then attacks this compound to form the final products. The failure in many cases to isolate these intermediates, together with the somewhat improbable nature of the compounds that

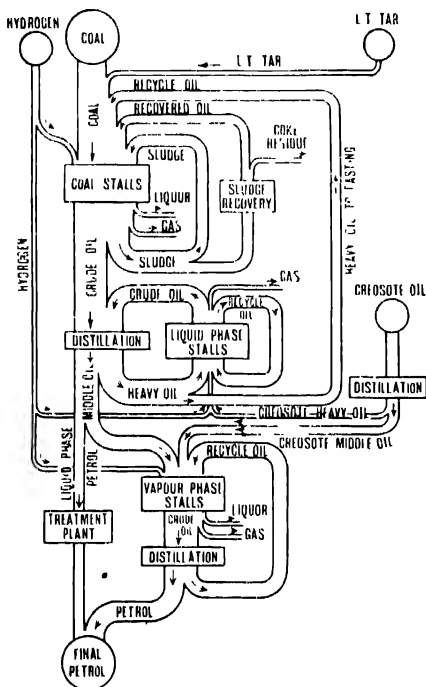


FIG. 8.

has substantially the same properties as that produced by coal hydrogenation.

### BIBLIOGRAPHY.

1. "Oil from Coal." K. Gordon, Trans. Inst. Mining Engineers, 1931-32, 82, 348.
2. "The Hydrogenation of Bituminous Coal." K. Gordon, Proc. World Petroleum Congress, London, 1933, 2, 317.
3. "Neue Fortschritte auf dem Gebiete der katalytischen Druckhydrierung." M. Pier, Proc. World Petroleum Congress, London, 1933, 2, 290.
4. "The Technique of Hydrogenation of Coal and its Products." King, J. Inst. Fuel, 1935-36, 9, 323.
5. J. G. King and J. Frazor Shaw, "Development of an Intermediate-Scale Plant for High-Pressure Hydrogenation of Tar and Tar Distillates." Chem. Eng. Congr., World Power Conference, 1936, iii, 463.
6. "The Development of Coal Hydrogenation by I.C.I." K. Gordon, J. Inst. Fuel, 1935-36, 9, 69.
7. "Synthetische Treibstoffe und Öle." Pier, World Petroleum Congress, Paris, 1937, 2, 1061.

in certain instances had to be postulated, caused this theory to fall into disrepute. More recently, however, it has been revived with a more liberal interpretation of the nature of the intermediate compounds. These are now regarded as special surface compounds, not necessarily having an existence independent of the surface. For example, in the adsorption of hydrogen on nickel a surface nickel-hydride is postulated, in which each hydrogen atom is bound to a nickel atom, and the remaining valency forces of the nickel atom are satisfied by its neighbours in and below the surface.

The most important advance in the theory of heterogeneous catalysis is due to Langmuir (J. Amer. Chem. Soc. 1916, **38**, 2268) who suggested that reaction occurs in a unimolecular layer of gas adsorbed on the catalyst. The concentration or fraction  $\theta$  of the surface covered by the gas was deduced as follows. The rate of evaporation of gas from the surface is proportional to the fraction of the surface covered, while the rate of condensation is proportional to the product of the free surface and the pressure  $p$  of the gas. At equilibrium these conditions give:

$$\theta = \frac{k_1 p}{k_2 + k_1 p}$$

At low surface concentrations,  $\theta$  is proportional to the pressure, while, when the surface is nearly saturated,  $\theta$  is independent of the pressure. The same general considerations, with modifications, hold if there are two gases. Thus, on this theory, if the rate of the reaction under examination is proportional to the surface concentration of a reactant, then the apparent order of reaction, as deduced from the dependence of the rate of reaction on the pressure in the gas phase, will vary between unity, when the gas is only slightly adsorbed, and zero, when the gas is strongly adsorbed. In this way observations of the order of reaction provide information as to the adsorption of the reactants on the catalyst, and this has been the main method used in the elucidation of reaction mechanisms (C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Clarendon P., Oxford, 1940. V. this vol., pp. 208-217).

The relationship between adsorption and catalytic activity has been explored at considerable length (G. M. Schwab, tr. by H. S. Taylor and R. Spence, "Catalysis from the Standpoint of Chemical Kinetics," Macmillan, 1937, Chap. 11). The observations of A. F. Benton and T. A. White (J. Amer. Chem. Soc. 1930, **52**, 2325) on the adsorption of hydrogen on nickel led to the concept of "activated adsorption" (H. S. Taylor, *ibid.* 1931, **53**, 578). At low temperatures, adsorption is rapid and does not involve high energies; the adsorbed molecules are not dissociated and are held to the surface by Van der Waals forces. At high temperatures, a slow adsorption occurs, involving a large energy of activation; this type of adsorption is known as activated adsorption. Taylor regards activated adsorption as being the formation of chemical bonds between the catalyst and the adsorbed molecule (chemisorption) and in general involving the dissociation of the mole-

culo (e.g. K. Morikawa, W. S. Benedict and H. S. Taylor, *ibid.* 1936, **58**, 1445). He considers that activated adsorption is intimately related to catalysis, and in many cases controls the rate of the catalytic reaction. There is, however, evidence that the phenomena of activated adsorption are more complex than is implied by this view, and may involve, for instance, solution in the bulk of the catalyst. On charcoal it appears that chemisorption may be a slow activated process, but, on the other hand, with metals it seems to be instantaneous and to require no energy of activation (J. K. Roberts, Proc. Roy. Soc. 1935, A, **152**, 445). The strength with which the chemisorbed layer is held suggests that the picture of catalysis as a two-dimensional gas reaction is incorrect. E. K. Rideal (Proc. Camb. Phil. Soc. 1939, **35**, 130) is of opinion that the essential feature of catalysis is the interaction between an adsorbed molecule held by Van der Waals forces with the chemisorbed layer. This does not imply that the Langmuir-Hinshelwood relationships between gas pressure and order of reaction no longer apply, for these will still apply to the Van der Waals layer and even to the chemisorbed layer at high temperatures.

Observations of the kinetics of reactions alone have not proved adequate to unravel the detailed mechanism, and more recently new techniques have been developed to deal with catalytic reactions. The reconversion of para- to ortho-hydrogen has been used as an indicator of the presence on the catalyst of atomic hydrogen (S. R. Craxford, Trans. Faraday Soc. 1939, **35**, 946). Reactions involving hydrogen-containing molecules can be further investigated by means of deuterium (exchange reactions) (A. Farkas, L. Farkas and E. K. Rideal, Proc. Roy. Soc. 1934, A, **146**, 630; K. Morikawa, W. S. Benedict and H. S. Taylor, *l.c.* and *ibid.* 1935, **59**, 1795). Several new lines of investigation into the nature of the catalysing surface and the adsorption of gases on it have been opened up. Among these may be mentioned the use of electron-diffraction to examine the lattice pattern of the surface (O. Beek, A. E. Smith and A. Wheeler, Proc. Roy. Soc. 1940, A, **177**, 62), the accommodation coefficient of neon on the surface as a means of studying the adsorbed film of gas (J. K. Roberts, *ibid.* 1932, A, **125**, 192; 1935, A, **152**, 445), the measurement of contact potentials (D. D. Eley and E. K. Rideal, *ibid.* 1941, A, **178**, 429), and the study of catalyst poisons in investigating the question of the uniformity of the surface (E. B. Maxted and H. C. Evans, J.C.S. 1938, 2071).

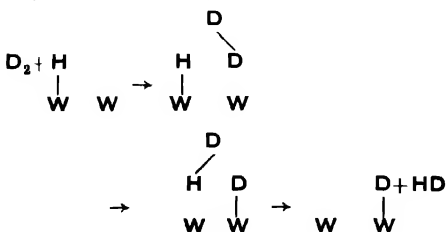
#### THE ORTHO-PARA HYDROGEN CONVERSION.

Before discussing actual examples of hydrogenation mechanism, it will be of interest to consider the interaction of hydrogen with the catalyst in the absence of a second type of molecule. Of all catalytic reactions the ortho-para conversion of hydrogen is the simplest (A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, 1935). These two forms of hydrogen differ only in that the atomic nuclei composing

the molecules have parallel spins in the one case and antiparallel spins in the other case. The catalytic interconversion of these two modifications can take place by two mechanisms. One of these, the low temperature mechanism, does not involve the separation of the atoms in the molecule. The catalyst used in this type of conversion is generally charcoal, and operates at temperatures below about 150°K. The conversion is ascribed to the existence of magnetic dipoles on the charcoal surface. The second type of ortho-para conversion, which is of greater interest in its bearing on catalytic hydrogenation, takes place generally on metallic catalysts and at higher temperatures—room temperature and above—though on specially active catalysts it has been detected at temperatures as low as 77°K. This type of conversion operates through the dissociation of the molecule into atoms. Exactly analogous to this latter reaction is the equilibration of light and heavy hydrogen,  $H_2 + D_2 \rightleftharpoons 2HD$ . The differences between the two reactions are small and are those expected from the greater mass of the heavy hydrogen. In the original mechanism proposed for these reactions (K. F. Bonhoeffer and A. Farkas, *Z. physikal. Chem.* 1931, B, 12, 231) the hydrogen molecules in their adsorption on the catalyst are dissociated into atoms. These atoms then recombine and evaporate as molecules, the recombination providing a chance for each atom to acquire a new partner. In this way, an equilibrium corresponding to the temperature of the catalyst is produced.

The validity of this explanation was brought into question by the work of J. K. Roberts (*Proc. Roy. Soc.* 1935, A, 152, 445) who showed that a clean tungsten surface on exposure to hydrogen is immediately covered with a complete film of the gas, which is present on the surface as atoms, and furthermore that this film shows no detectable sign of evaporation at room temperature. The extreme stability of the adsorbed hydrogen and the high energy required to bring about evaporation militate against the explanation of Bonhoeffer and Farkas.

According to an alternative explanation suggested by E. K. Rideal (*Proc. Camb. Phil. Soc.* 1939, 35, 130), conversion (or equilibration) takes place through an interchange between an adsorbed hydrogen atom and a molecule adsorbed above the atomic layer. In the case of the reaction  $H_2 + D_2 \rightleftharpoons 2HD$  the scheme is as follows:



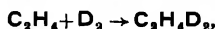
This explanation demands a certain fraction of gaps in the atomic layer; this has been shown to exist, as the surface is bare to the extent of 8% (J. K. Roberts, *loc. cit.* p. 464). It will be seen

that this mechanism leaves the total amount of hydrogen on the surface unaltered and enables the reaction to proceed with much less energy than would be required for the evaporation of molecules. An experimental proof of this mechanism has now been devised (D. D. Eley and E. K. Rideal, *Proc. Roy. Soc.* 1941, A, 178, 429). Clean tungsten films, prepared by evaporation, were found to bring about the equilibrium  $H_2 + D_2 \rightleftharpoons 2HD$  in a few minutes at 77°K. A clean film was brought in contact with deuterium and then thoroughly pumped out at room temperature. After being cooled to 77°K, it was exposed to a low pressure of light hydrogen, when an interchange of light and heavy hydrogen was observed in a time similar to that required for attainment of the equilibration  $H_2 + D_2 \rightleftharpoons 2HD$ . This can only have taken place through such a mechanism as that outlined above. It follows from the mechanism of these reactions that the ortho-para conversion and the equilibration reaction can be used to indicate the presence or absence of atomic hydrogen on a catalyst.

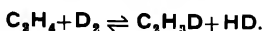
#### THE HYDROGENATION OF ETHYLENE.

The catalytic addition of hydrogen to substances containing an ethylenic double bond is probably the most important type of hydrogenation. The simplest of these reactions was discovered by P. Sabatier and Senderens (*Compt. rend.* 1897, 124, 1359) who showed that in the presence of nickel, ethylene could be quantitatively hydrogenated to ethane. Later it was found that a number of other metals, notably copper, platinum, cobalt and iron, were effective as catalysts; nickel, however, remains the chief catalyst in practice. Although the hydrogenation of ethylene has been intensively studied since 1897, the mechanism of the process is still not completely explained, and it is only of recent years, through the discovery of deuterium, that the necessary means for its elucidation have become available. Earlier attempts were made to find the mechanism by a study of kinetics and the application of Langmuir's theory. Pease (*J. Amer. Chem. Soc.* 1923, 45, 1196) found that on copper the rate of reaction was proportional to the hydrogen pressure, but decreased as the ethylene pressure increased. From this it was deduced that the hydrogen was weakly adsorbed, whereas the ethylene was so strongly adsorbed that it tended to displace the hydrogen from the surface. Rideal (*J.C.S.* 1922, 121, 309), using nickel, found that at high ethylene concentrations the hydrogen displaced the ethylene. Many other investigations have given similar results, and all show that the ethylene is very strongly adsorbed and the hydrogen only weakly adsorbed. Further progress along this line was not possible.

**The Exchange Reaction between Ethylene and Deuterium.**—A new approach to the problem was opened up by the discovery of A. Farkas, L. Farkas and E. K. Rideal (*Proc. Roy. Soc.* 1934, A, 146, 630) that when ethylene interacted with deuterium on a nickel catalyst, in addition to the normal hydrogenation,



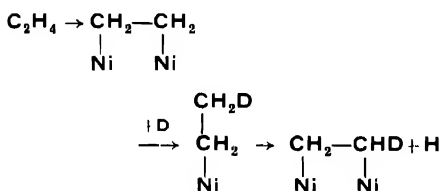
there also occurred an exchange reaction between the deuterium and the light hydrogen of the ethylene; this may be formulated:



This exchange reaction offered a means of investigating the state of the ethylene adsorbed on the catalyst. Two mechanisms for this reaction are possible:

(1) *Dissociative Mechanism*.—In this, it is supposed that on adsorption the ethylene molecule is split up into a hydrogen atom and a  $\text{C}_2\text{H}_3$  fragment, and the deuterium is dissociated into atoms. Exchange takes place through the addition of one of these deuterium atoms to a  $\text{C}_2\text{H}_3$  fragment, and the consequent desorption of a substituted ethylene molecule.

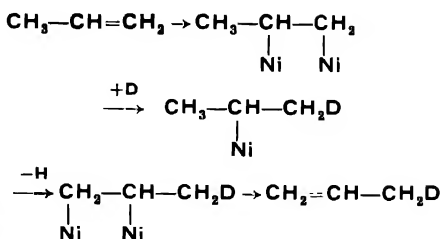
2. *Associative Mechanism*.—Assuming this mechanism (I. Horiuti and M. Polanyi, *Trans. Faraday Soc.* 1934, **30**, 1164) to operate then ethylene is adsorbed on the catalyst by the opening of the double bond and attachment of the molecule to two nickel atoms. A deuterium atom then adds on to give a nickel-ethyl radical which breaks up to reform an adsorbed ethylene molecule and liberates a light hydrogen atom. This mechanism can be represented as follows:



The balance of the evidence suggests that this second mechanism is the correct one. The low temperatures at which exchange between ethylene and deuterium occurs are in contrast to the high temperatures required for exchange with ethane, which can only proceed through a dissociative mechanism. A direct test was made (G. K. T. Conn and G. H. Twigg, *Proc. Roy. Soc.* 1939, A, **171**, 70) by examining the possibility of exchange between light ethylene ( $\text{C}_2\text{H}_4$ ) and heavy ethylene ( $\text{C}_2\text{D}_4$ ) in the absence of hydrogen. On the dissociative mechanism, the ethylenes should on adsorption be broken down into  $\text{C}_2\text{H}_3$  and  $\text{C}_2\text{D}_3$  fragments, and hydrogen and deuterium atoms; on recombination and evaporation, exchange should occur with the formation of compounds of the type  $\text{C}_2\text{H}_3\text{D}$ ,  $\text{C}_2\text{H}_2\text{D}_2$ , etc. Analysis, effected by means of the infra-red absorption spectra of the ethylenes, showed no exchange.

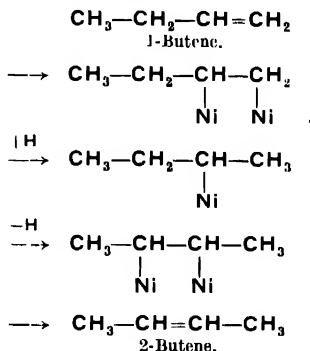
Further evidence in favour of the associative mechanism was obtained by examination of the exchange reactions of the higher olefins (G. H. Twigg, *Trans. Faraday Soc.* 1939, **35**, 934). On the dissociative mechanism, one might expect that the hydrogen atoms not immediately attached to the double bond would be no more reactive for exchange than those of ethane. On the associative mechanism, however, all the hydrogen atoms ought to be equally reactive. For example, in the case of propene the

associative mechanism gives the following picture:



In this way a deuterium atom can be introduced into the methyl group. The equivalence of the hydrogen atoms in a number of substituted ethylenes has been demonstrated.

In a similar manner the migration of the double bond, which occurs in higher olefins when they are brought into contact with a catalyst in the presence of hydrogen (G. H. Twigg, *Proc. Roy. Soc.* 1941, A, **178**, 106), is more readily explicable if one assumes the associative mechanism for exchange. For example, in the case of the isomerisation of 1-butene to 2-butene, the scheme of reaction is:

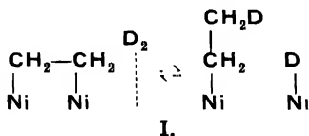


No double bond migration was found in the absence of hydrogen. Other evidence in favour of the associative mechanism for exchange was obtained from a consideration of the energies of activation of the various reactions.

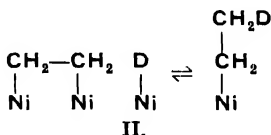
This proof of the mechanism of exchange gave the first clue to the process of adsorption of ethylene on the catalyst surface. Before this is discussed more fully, however, there is the question of the adsorption of the hydrogen to be considered. On an active hydrogenating catalyst, the ortho-para-hydrogen conversion is very fast at room temperature. By using para-hydrogen in the hydrogenation of ethylene, it was shown that the ethylene completely prevented the ortho-para conversion, although a rapid hydrogenation occurred. Similarly, when deuterium was used, the equilibration reaction  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$  was found to be inhibited up to about 140°C. These observations confirm that the ethylene is strongly adsorbed, covering most of the catalyst surface, and also show that there is practically no atomic hydrogen on the surface. The kinetics of the

exchange and hydrogenation reactions were studied simultaneously and found to be identical, the rate of reaction in both cases being independent of the ethylene pressure and proportional to the first power of the hydrogen or deuterium pressure (G. H. Twigg and E. K. Rideal, *ibid.* 1939, A, 171, 55). It had been expected that since hydrogenation requires two atoms of hydrogen and exchange only one atom, the rate of exchange would be proportional to the square root of the hydrogen pressure. Since it was not so, the slow step in exchange must involve the undissociated molecule.

To explain all these results, it was assumed that the first step in exchange was a reaction involving a deuterium molecule adsorbed in the Van der Waals layer above the chemisorbed ethylene layer. This can be depicted as:

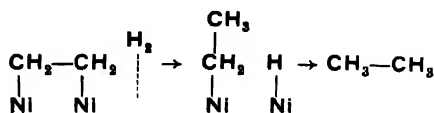


To explain the state of equilibrium of the hydrogen-deuterium mixture during reaction, it is necessary to assume another step, faster than (I):



In this way a fairly complete picture of the exchange reaction has been obtained. From the close resemblance in the kinetics of the hydrogenation and exchange reactions, including the fact that the energy of activation for both reactions decreases at high temperatures, it appears that the state of adsorption of the gases is the same in both reactions. That is, hydrogenation involves the interaction of an undissociated hydrogen molecule adsorbed by Van der Waals forces with an ethylene molecule chemisorbed at two points by opening the double bond.

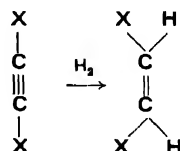
**Addition of Hydrogen to the Double Bond and the Acetylenic Triple Bond.**—Since exchange proceeds through the associative mechanism, there are two ways in which hydrogenation of ethylene to ethane can be effected. The first involves the separate addition of two atoms (I. Horiuti and M. Polanyi, *l.c.*). The first atom adds on to form the intermediate nickel-ethyl complex as in the exchange reaction, but instead of this breaking down to re-form an adsorbed ethylene molecule, a second hydrogen atom may add on to it and form ethane, according to the following scheme:



The alternative mechanism for hydrogenation does not require the formation of the nickel-ethyl complex. The hydrogen molecule is presumed to add directly to the adsorbed ethylene without preliminary dissociation.

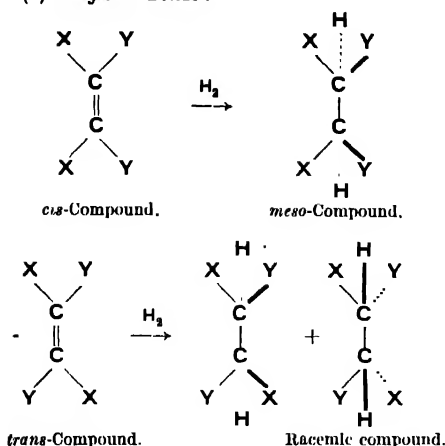
A considerable body of evidence, mostly indirect however, points to the second hypothesis as the true one. The first piece of evidence in favour of molecular addition was put forward by G. Vavon (Bull. Soc. chim. 1927, iv), 41, 1253) who pointed out that in the catalytic hydrogenation of conjugated double bonds no 1:4 addition occurred, whereas if hydrogenation was effected by nascent hydrogen, addition of two atoms of hydrogen in the 1:4 positions was usually found. The main evidence for molecular addition, however, rests on the formation of stereochemical isomers by hydrogenation. A comprehensive survey of the literature has been made by A. and L. Farkas (Trans. Faraday Soc. 1937, 33, 837). These authors show that the hypothesis of molecular addition holds not only for ethylenic bonds, but also for acetylenic triple bonds. It is assumed that if the hydrogen molecule adds as a whole without previous dissociation, then addition takes place in the *cis*-position. The schemes of reaction are as follows:

(1) *Acetylenic Bonds*:



By this mechanism the addition of a molecule of hydrogen to an acetylenic compound will produce a *cis*-ethylenic derivative. If on the other hand the addition of hydrogen proceeds atom by atom, then both *cis*- and *trans*-derivatives can be formed, and the product will be the thermodynamically most stable mixture of the two; in general, since *trans*-compounds are usually the more stable, the result of atomic addition will be the *trans*-derivative. One point has to be noticed, however. There is the possibility of a *cis-trans*-isomerisation taking place on the catalyst in the presence of hydrogen, by the mechanism discussed above for double-bond migration and exchange. This would tend to cause the attainment of the thermodynamic equilibrium. Since exchange is known to be faster than hydrogenation at high temperatures, this *cis-trans*-isomerisation would be expected to be marked at high temperatures. Thus, if hydrogenation is molecular, the products of reaction ought, in general, to be the *cis*-ethylenic derivative at low temperatures, and the *trans*-derivative at high temperatures or when nascent hydrogen has been used. The observations of A. and L. Farkas support this. For example, toluene on catalytic hydrogenation forms the *cis*-compound isostilbene, whereas with nascent hydrogen it yields stilbene; phenylpropionic acid is hydrogenated on a catalyst to isocinnamic acid, but with nascent hydrogen yields cinnamic acid.

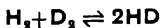


(2) *Ethyleneic Bonds*:


In these diagrams the dotted lines indicate bonds below the plane of the paper, and the heavy lines bonds above. From this scheme it is seen that low temperature catalytic hydrogenation should yield a racemic mixture from a *trans*-compound, and a *meso*-compound from a *cis*-compound, whereas at high temperatures or with nascent hydrogen the most stable form will be produced, which is, in general, the *meso*-compound. These predictions were confirmed. For example, the catalytic hydrogenation of *cis*- and *trans*-dimethylstilbene yielded the *meso*- and racemic products respectively. Again, when *ortho*- and *para*-xylene are hydrogenated at room temperature, they yield mainly *cis*-1:2-dimethylcyclohexane and *cis*-1:4-dimethylcyclohexane respectively; but if the hydrogenation is carried out at 180°C., the *trans*-compounds are produced in both cases (A. Farkas, *ibid.* 1939, 35, 906).

From these observations, therefore, our present picture of the mechanism of hydrogenation is obtained. The olefin is adsorbed on the catalyst by the opening of the double bond and the formation of two nickel-carbon bonds; the hydrogen is adsorbed on top of this film in the molecular state. When the hydrogen molecule reacts with the nickel-carbon bond, exchange results (see I, p. 376a), and when it reacts with the carbon carbon bond, addition takes place and the saturated compound is formed.

One feature of hydrogenation which is still obscure is the reduction in the energy of activation which takes place at high temperatures and which may produce a diminution in the rate of reaction with increasing temperature. The most reasonable explanation of this phenomenon is that it is due to desorption or displacement of the olefin from the catalyst by hydrogen (H. zur Strassen, Z. physikal. Chem. 1934, A, 169, 81), though this does not agree with the observation (Twigg and Rideal, Proc. Roy. Soc. 1939, A, 171, 55) that the reaction

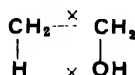


is inhibited at temperatures above those at which the decrease in energy of activation sets in

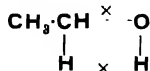
and L. Farkas (J. Amer. Chem. Soc. 1938, 60, 22) have suggested that this decrease is due to an increase with temperature in the concentration of the dissociated fragments ( $\text{C}_2\text{H}_2$  in the case of ethylene), these fragments not being available for hydrogenation to ethane. If this is so, the energy of activation for exchange should show no decrease with increasing temperature. Twigg and Rideal (*l.c.*) have, however, found a decrease for exchange parallel to that for hydrogenation.

## CATALYST STRUCTURE AND THE CHEMISORPTION OF OLEFINS.

The lattice spacing of the catalyst and the fitting of the adsorbed reactants to the catalyst are of considerable importance in view of the specificity of catalysts and the marked effect of traces of promoters in increasing the rate of reaction. The effect of small alterations of the interatomic distances on the surface has been pointed out by A. Sherman and H. Eyring (J. Amer. Chem. Soc. 1932, 54, 2661), who calculated the energy of activation for the adsorption of hydrogen on charcoal at varying carbon-carbon distances. They found that with a carbon-carbon distance of 3.6 Å. the energy was a minimum, but that on either side of this distance the energy required rose rapidly. The importance of the way in which the reactant is adsorbed was stressed by A. A. Balandin (Z. physikal. Chem. 1929, B, 2, 289) who considered that one catalyst atom could adsorb two atoms or radicals of the reactant, thereby causing these atoms or radicals to combine (the multiplet hypothesis). For example, certain oxide catalysts cause the simultaneous dehydration and dehydrogenation of alcohol. Balandin suggested that when the alcohol was adsorbed as shown:



it was dehydrated to ethylene (the crosses represent catalyst atoms). But if it was adsorbed as



the products were acetaldehyde and hydrogen. This concept was extended further to the dehydrogenation of cyclohexane. The reacting molecules are presumed to be adsorbed on the hexagonal lattice of the catalyst (fig. 1). The catalyst atoms 1, 2 and 3 each hold two carbon atoms of the cyclohexane, while the atoms 4, 5 and 6 each attract a pair of hydrogen atoms and cause them to combine. Similarly in hydrogenation the benzene molecule might be adsorbed in the same manner and the hydrogen molecules adsorbed on the atoms 4, 5 and 6 would then add across the bonds *a-b*, etc.

An important contribution to the question of the effect of the lattice structure of the catalyst on its activity has been made by O. Beek, A. E. Smith and A. Wheeler (Proc. Roy. Soc. 1940, A, 177, 62). These authors prepared

evaporated metal films which had different crystal planes exposed to the gas phase. The crystal structure of these films was investigated by electron diffraction. Two types of nickel film could be prepared, one completely oriented with the (110) crystal plane parallel to the surface on which the film was deposited, and the other with a random orientation. The activity of these films was measured by the hydrogenation of ethylene. It was found that the oriented film was 5 times as active as the unoriented film. Thus the (110) plane, the least densely packed plane, appears to be more

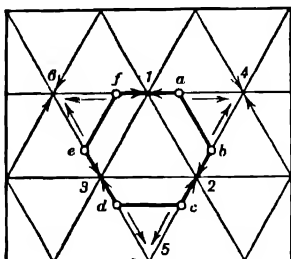


FIG. 1.

favourable for hydrogenation than either the (100) or the (111) plane.

Another approach to this problem has been made by G. H. Twigg and E. K. Rideal (Trans. Faraday Soc. 1940, **36**, 533) who made the mechanism for exchange the basis of calculations on the fitting of olefins to the catalyst. When the olefin is chemisorbed on the catalyst, the double bond is opened and attachment takes place between the two carbon atoms of the double bond and two nickel atoms. The first calculation concerned the fitting of the olefin molecule between the two nickel atoms (fig. 2).

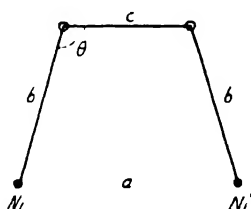


FIG. 2.

There are two nickel-nickel distances in the nickel crystal, the distance of closest packing, 2.47Å., and the unit cell side, 3.50Å. The latter was found to be too great to accommodate the olefin molecule as postulated. In fig. 2 an adsorbed ethylene molecule is drawn to scale. The Ni-Ni distance (*a*) is 2.47Å., the C-C distance (*c*) is 1.52Å., equal to the normal single bond distance, and the Ni-C bond distance (*b*) is assumed to be equal to that in nickel carbonyl. The molecule fits very well, the angle  $\theta$  being distorted slightly from the tetrahedral angle  $109^\circ 28'$  to  $105^\circ 4'$ . This distortion can be made less if the C-C axis is made to lie at a small

angle to the Ni-Ni axis. The effect of promoters on catalytic activity may be due to small distortions of the crystal lattice causing a more favourable interatomic distance. The interatomic distance appears to be an important factor in determining the activity of the catalyst. In the chemisorption of olefins, as described here, the maximum possible interatomic distance in the catalyst appears to be about 2.8Å., which may explain why those catalysts active in hydrogenation have interatomic distances of closest approach between 2.47Å. and 2.54Å. (Fe, Ni, Co, Cu) and between 2.7Å. and 2.8Å. (Pt, Pd). In the latter group the form of the crystal lattice is important, only those metals having a face-centred cubic lattice being active in hydrogenation.

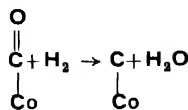
Another calculation was made on the interaction of neighbouring adsorbed molecules. A plan, drawn to scale, of the nickel surface with adsorbed olefin molecules is shown in fig. 3. Two cases are shown: A, adsorption on the (111) plane and B, on the (110) plane. For the ethylene molecule, the hydrogen atoms have been drawn to scale (full circles). There is slight interaction between neighbouring molecules on the (111) plane, though this is probably insufficient to prevent them covering the whole surface. On the (110) plane there is no interaction, and thus ethylene can cover the whole surface. This is in agreement with the fact that ethylene inhibits the reaction  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ . The case of the methyl-substituted ethylenes is different, however. The methyl groups are drawn to scale (dotted circles, fig. 3). Here the interaction between neighbouring atoms is quite considerable even on the (110) plane, and these molecules should not be capable of covering the whole surface. That this is actually so is shown by the fact that the equilibration  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$  still proceeds in the presence of 2-methylpropene or 2-methyl-2-butene; again, in the hydrogenation of butene, the rate of reaction is not independent of the butene pressure. In this way confirmation of the general picture of the adsorption of olefins has been obtained. The fitting of the molecule to the catalyst is probably the cause of selective hydrogenation in the case of complex molecules containing more than one double bond.

#### THE FISCHER-TROPSCH SYNTHESIS.

In the field of catalytic hydrogenation, one of the most important reactions is the Fischer-Tropsch synthesis of long chain paraffin and olefin hydrocarbons from carbon monoxide and hydrogen. The type of catalyst used consists of iron, nickel or cobalt with a suitable promoter and support. Investigations into the mechanism of the reaction have been made with a catalyst which consists of cobalt, thorium and kieselguhr in the proportions 100:18:100; cobalt and thorium carbonate are precipitated on the kieselguhr and reduced in hydrogen at  $375^\circ\text{C}$ . (Report of the Fuel Research Board, 1938, 189). The general characteristics of the reaction are as follows (F. Fischer, Ber. 1938, **71** [A], 56). When the synthesis gas, 1 part of carbon monoxide and 2 parts of hydrogen, is

passed over the freshly reduced catalyst at 190°C. and atmospheric pressure, methane and carbon dioxide are formed. After some time the Fischer synthesis sets in and the products are oil and water. The temperature range over which the oil synthesis occurs is small. Below 175°C. there is no reaction; between 175°C. and 225°C. oil is produced, and above 225°C. the main products are methane and carbon dioxide. At high pressures, oxygen-containing substances are formed as well as the hydrocarbon oils. Investigations into the mechanism (S. R. Craxford, *Trans. Faraday Soc.* 1939, **35**, 946) show that the reaction takes place through the formation on the catalyst of cobalt carbide. Evidence for this is that a used catalyst, when decomposed by hydrochloric acid, yielded a mixture of paraffins and olefins. Measurements of the electrical conductivity of the catalyst during synthesis showed that carbide was being formed in increasing amounts as the synthesis proceeded. Craxford showed that the forma-

tion of carbide does not occur through the reaction  $2\text{Co} + 2\text{CO} \rightarrow \text{Co}_2\text{C} + \text{CO}_2$ , because this reaction is slower than either the reduction of carbide to methane or the Fischer-Tropsch synthesis; this reaction would thus not allow carbide to accumulate on the catalyst. The reaction postulated for carbide formation is the reduction of a surface carbonyl:



Evidence for this is that the oxygen product of the synthesis is water and not carbon dioxide. This water cannot have come from the reaction  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  as the equilibrium of this reaction is entirely on the carbon dioxide side at 200°C.

By using para-hydrogen in the synthesis gas

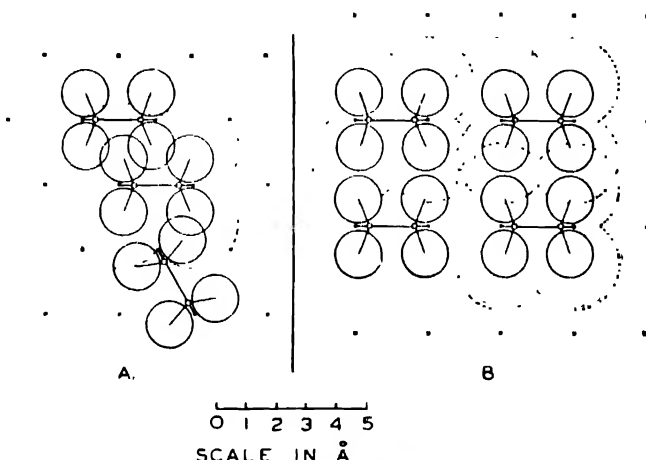
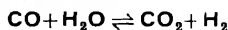


FIG. 3.—PLAN OF CHEMISORBED ETHYLENE AND METHYLETHYLENES ON THE NICKEL SURFACE.

instead of normal hydrogen, the ortho-para-hydrogen conversion could be measured simultaneously with the synthesis. At 200°C. when synthesis to give oil was taking place, no ortho-para conversion was detectable. Under other conditions, below 160°C. when no reaction occurred, or during the running-in of a catalyst when the products were methane, carbon dioxide and carbide, or at 200°C. with hydrogen in great excess when only methane was formed, or at temperatures above 250°C. where the product is entirely methane, the ortho-para conversion occurred freely. As has been pointed out, the occurrence of the ortho-para conversion may be taken as an indication of the presence of hydrogen atoms on the catalyst. Hence, it is concluded that when the Fischer oils are being produced there is little, if any, atomic hydrogen on the catalyst, whereas the production of methane is associated with the presence on the catalyst of atomic hydrogen.

The water-gas reaction



exhibits a behaviour parallel to that of the ortho-para conversion. At 200°C. the equilibrium is almost entirely on the right-hand side, yet during the synthesis of oil, the oxygen product is mainly water with only a trace of carbon dioxide. But under the conditions where the synthesis yields methane instead of oil, the water-gas reaction occurs and carbon dioxide is formed instead of water. Thus this reaction is determined by the same conditions as determine the ortho-para-hydrogen conversion.

From these observations, it is considered that the second step in the synthesis is the reduction of the carbide by molecular hydrogen leading to the production of  $\text{CH}_2$  groups chemisorbed on the cobalt. When atomic hydrogen is present on the catalyst, the  $\text{CH}_2$  groups are hydro-

generated to methane. In the absence of atomic hydrogen, the groups link up with each other to form long paraffin chains. That this linking-up process is more probable than a mechanism involving the addition of carbon monoxide to the end of a chain followed by reduction, is shown by the fact that cobalt carbide on treatment with dilute acid gives rise to long-chain hydrocarbons.

The mechanism whereby the  $\text{CH}_2$  groups link up is not completely understood. E. F. G. Herington (Trans. Faraday Soc. 1941, **37**, 361) has calculated that the acetylene molecule can be adsorbed on the nickel or cobalt lattice across the 3.50 Å. distance by the transformation of the triple into a double bond. This is in contrast to ethylene which can only be adsorbed across the shorter 2.47 Å. distance. It is found that if acetylene is added to the synthesis gas in the Fischer-Tropsch reaction, it polymerises in-

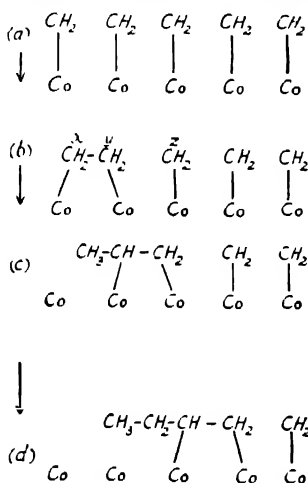


FIG. 4.

dependently, and is not incorporated in the Fischer oil produced. On the contrary, if ethylene is present in the ingoing gas, it is incorporated into the products. This gives grounds for thinking that the combination of the  $\text{CH}_2$  groups during synthesis occurs across the short spaces of the cobalt lattice. From spatial considerations, it can be seen that during the linking-up to form a large molecule, the individual  $\text{CH}_2$  groups cannot remain attached to their original catalyst atoms by Van der Waals forces. Consequently the scheme of reaction shown in fig. 4 has been proposed. This mechanism finds support in the fact that the products of the Fischer-Tropsch synthesis contain a large quantity of olefins with the double bond in the terminal position.

#### CATALYST UNIFORMITY.

The question of the uniformity of catalysts has not yet been decided satisfactorily, though it appears that there must be areas of different activity. The concept of active centres is largely due to H. S. Taylor (J. Physical Chem.

1928, **30**, 145) who considers these centres to be atoms or groups of atoms projecting above the plane of the catalyst and having a high activity by virtue of their instability. The evidence for and against this concept is mostly indirect. In its favour the fact is quoted that the heat of adsorption of a gas on the catalyst decreases with the amount adsorbed (H. S. Taylor, Z. Elektrochem. 1929, **35**, 545), and the fact that poisons reduce the activity of catalysts many-fold while the adsorption is only slightly affected. Arguments from adsorption, however, may not be entirely conclusive since adsorption can be composed of several factors, chemisorption, Van der Waals adsorption and solution in the mass of the catalyst, of which the first only is concerned in catalysis; varying heats of adsorption have been explained as due to interaction between neighbouring adsorbed atoms or molecules (K. F. Herzfeld, J. Amer. Chem. Soc. 1929, **51**, 2608). More valid evidence, however, is derived from cases in which two simultaneous reactions are possible with the same catalyst and reactants. When allyl alcohol vapour is passed over heated copper, it may either isomerise to propionaldehyde or be dehydrogenated to acrolein. F. H. Constable (Proc. Roy. Soc. 1926, A, **113**, 254) showed that the ratio in which the two reactions occurred was dependent upon the method of preparation of the catalyst. Many other examples of this kind have been found. Against the theory of active centres is the observation of E. W. R. Steacie and E. M. Elkin (*ibid.* 1933, A, **142**, 457) that there was no discontinuity in activity at the melting-point of zinc when this metal was used as a catalyst in the decomposition of methyl alcohol between 360° and 440°C. E. B. Maxted and his co-workers (J.C.S. 1933, 502; 1934, 26, 672; 1935, 393, 1190) re-investigated the work of Vavon and Husson (Compt. rend. 1922, **175**, 277) on the effect of poisons on the hydrogenation of different organic substances, and found that the relative reduction in the rate of hydrogenation was the same in all cases, even when the absolute rates differed considerably. Thus the same parts of the catalyst appear to be concerned in the different types of hydrogenation. Other evidence of catalytic homogeneity comes from the fact that the energy of activation for the hydrogenation of crotonic acid is the same on a fresh catalyst and on one of which the activity has been reduced by sintering or by poisoning. Other experiments using catalyst poisons point to the uniformity of the surface (Maxted and Evans, J.C.S. 1937, 1004; 1938, 2071). The comparative toxicities of hydrogen sulphide and various alkyl thiols and sulphides to a platinum catalyst were measured. It was found that the toxicity of the sulphides was more than twice that of the thiols, and in both series of compounds the toxicity increased with the length of the alkyl chain. The ratio of the toxicities of methyl sulphide and hydrogen sulphide was 9.0:1. If these molecules are presumed to be anchored to the surface by the sulphur atom, then by drawing a scale model of these molecules on the surface, it can be seen that while the hydrogen sulphide occupies one platinum atom, the methyl sulphide molecule

can cover nine atoms. Thus, over small areas, the catalyst is uniform. These experiments also show two types of catalyst surface, each in itself homogeneous. The work of Boeck, Smith and Wheeler (Proc. Roy. Soc. 1940, A, 177, 62) shows in another way that different types of surface can be present in the catalyst. The present position thus appears to be that while the catalyst may contain different types of surface, there is no evidence for isolated centres of high activity such as those postulated by Taylor, and the surface must be regarded as made up of areas of relatively uniform activity.

G. H. T.

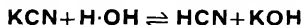
**HYDROLITH.** A technical name for calcium hydride,  $\text{CaH}_2$  (*v.* Vol. II, 205*d*, and this Vol., p. 330*b*). Hydrolith has commercial importance as a reducing agent in metallurgy, and for generation of hydrogen by interaction with water, 1 kg. producing about 1 cu. m. of the gas at ordinary temperatures and pressures. For technical applications, see Alexander, Met. & Alloys, 1937, 8, 263; 1938, 9, 45.

**HYDROLYSIS.** The term hydrolysis (or hydrolytic dissociation) is given to a number of different chemical reactions, all of which consist in the addition of water to a complex, and the subsequent resolution of the product into simpler substances.

Some of the best-known types of hydrolysis are those of metallic salts, esters, acid chlorides, amides, etc., or generally acyl derivatives, complex carbohydrates and glycosides, and finally, polypeptides and proteins.

#### 1. HYDROLYSIS OF SALTS.

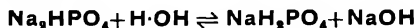
The hydrolysis of a salt by water may be represented by means of an equation of the type :



The reaction is a balanced one, and may be regarded as due to the incomplete neutralisation of the acid and base from which the salt is derived; in terms of the ionic theory the acid in question (HCN) does not yield sufficient hydrions to combine with the hydroxyl ions of an equivalent quantity of the strong base (KOH). When equivalent quantities of a strong acid and a strong base are brought together in aqueous solution complete neutralisation takes place, and a normal salt with a neutral reaction towards common indicators is formed. (Basis of methods of acidimetry and alkalimetry.) In the cases of such salts appreciable hydrolysis would not be expected even in dilute solution. The following are the common types of salts which are hydrolysed by water: (1) salts derived from feeble acids and strong bases; (2) salts from strong acids and feeble bases; (3) salts from feeble acids and feeble bases. Examples of the first type are potassium cyanide (*v.s.*) and sodium phosphate,

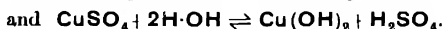


and even

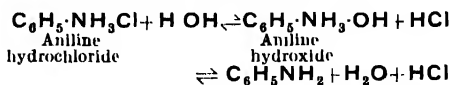


Solutions of such salts invariably have an alkaline reaction towards common indicators, *e.g.* litmus, phenolphthalein. The water may

be regarded as a feeble acid, which, like any other feeble acid, liberates a certain amount of acid from the salt with which it is brought into contact. In many cases acid salts are first formed, *e.g.* sodium phosphate, sodium carbonate, but free acid and free base may be liberated. The alkaline reaction of the solution can be accounted for by the fact that the feeble acid, or the acid salt formed, is ionised to a slight extent only, whereas with moderately dilute solutions the strong base is almost completely ionised, and thus there is a great excess of hydroxyl ions over hydrions. Examples of the second type are ferric chloride and cupric sulphate, which are derived respectively from the feeble bases, ferric hydroxide and cupric hydroxide. The aqueous solutions of such salts invariably give an acid reaction. The hydrolysis may be represented by means of the equations :



With moderately concentrated solutions basic salts, *e.g.*  $\text{FeCl}_2\text{OH}$  are almost certainly formed, and it is only in very dilute solution that the hydrolysis will proceed to the formation of the metallic hydroxide, and even when this is formed it is not precipitated, but remains in solution in the form of a colloid. A group of salts which belongs to this type is that of the salts derived from the strong mineral acids, and feeble organic bases such as aniline, *e.g.*



Examples of the third type are ferric phosphate, aluminium carbonate and sulphide and aniline acetate. The hydrolysis in the first case is readily shown by washing finely divided ferric phosphate with distilled water, when it is found that the filtrate is always distinctly acid, owing to the free phosphoric acid which has been washed away by the water, and if the operation is continued nearly pure ferric hydroxide remains on the filter. In the case of the two aluminium salts, they are so readily hydrolysed that when brought into contact with water they yield the corresponding metallic hydroxide, and the free acids, carbonic acid and hydrogen sulphide, which escape and thus destroy the equilibrium.

In the case of salt formation we may regard the water as capable of acting as either a feeble base or a feeble acid. When in contact with equivalents of a strong acid and a feeble base the water competes with the base for the acid, and hence neutralisation is not complete, or, in other words, hydrolysis of the salt occurs and the feeble base the greater the degree of hydrolysis. The mechanism of salt hydrolysis according to the ionic theory is as follows: In aqueous solution the given salt, *e.g.* potassium cyanide, is ionised in the ordinary manner into  $\text{K}^+$  and  $\text{CN}^-$  ions, but water itself is ionised to a slight extent,  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ , and as hydrogen cyanide is a very feeble acid, and therefore

ionised to only a very slight extent in aqueous solution, there is a tendency for the  $H^+$  ions of the water to combine with the  $CN^-$  ions from the cyanide, yielding undissociated  $HCN$ ; the result is that the equilibrium  $H_2O \rightleftharpoons H^+ + OH^-$  is destroyed and more molecules of water are ionised, but this results in further combination between  $H^+$  and  $CN^-$  ions, and by this means an excess of  $OH^-$  over  $H^+$  ions is produced, and thus the alkaline reaction. The changes continue until ultimately equilibrium is established between the  $KCN$ ,  $CN^-$ ,  $K^+$ ,  $H^+$ ,  $OH^-$ ,  $HCN$  and  $H_2O$  present. The degree of hydrolysis, i.e. the fraction of the salt hydrolysed, cannot be determined by direct titration of the free acid or free base present in solution; the addition of standard acid to the solution of potassium cyanide would immediately destroy the equilibrium which previously existed, and more salt would be hydrolysed in order to restore the equilibrium, and the point of neutrality would not be reached until acid sufficient to decompose the salt completely had been added. The methods commonly adopted for determining the degree of hydrolysis are (see Farmer, B. A. Report, 1904, 240): (1) Determination of the concentration of the free acid or free alkali present in the solution of the salt by its catalytic effect on the hydrolysis of an aqueous solution of ethyl acetate or on the inversion of a solution of cane sugar, and then determining the amount of pure acid or alkali required to produce the same effect (for acid, see Walker, Z. physikal. Chem. 1889, 4, 319; for alkali, see Shields, *ibid.* 1893, 12, 107; also Bruner, *ibid.* 1900, 32, 133; Ley, *ibid.* 1899, 30, 216; Walker and Aston, J.C.S. 1895, 67, 576). (2) Determination of the electrical conductivity of the solution (Walker, Z. physikal. Chem. 1889, 4, 333; Bredg, *ibid.* 1894, 13, 313; Lundy, J. Chim. Phys. 1907, 5, 574; Denham, J.C.S. 1908, 93, 41). The molecular conductivity of a hydrolysed salt of the type aniline hydrochloride is made up of two quantities: (a) conductivity due to the non-hydrolysed salt; (b) conductivity due to the free acid formed on hydrolysis—since the free base (aniline) is not an electrolyte.  $M = (1-x)u_1 + xv_{HCl}$ , where  $M$  = molecular conductivity,  $x$  = degree of hydrolysis,  $u_1$  = molecular conductivity of non-hydrolysed salt and  $v_{HCl}$  that of the free acid formed. The various quantities in the equation with the exception of  $x$  can be determined and then  $x$  calculated. (3) Determination of the partition coefficient (Farmer, *ibid.* 1901, 79, 863). In the case of the hydrolysis of aniline hydrochloride the concentration of the free base is determined by shaking the aqueous solution at a given temperature with a known volume of benzene, and finding the concentration of the aniline in the benzene layer. Since  $C_B/C_A$  is always constant ( $C_B$  = concentration of aniline in benzene and  $C_A$  = concentration of aniline in water) for a given temperature the concentration of free aniline in the aqueous layer can be calculated directly, and thus the degree of hydrolysis determined. The assumption is made that the salt present does not affect the partition coefficient to an appreciable extent. (4) Observing the change in colour produced by a solution of the hydrochloride of an organic

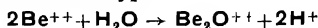
base in a solution of Methyl Orange of known concentration, and a comparison of this change with that produced by the addition of known quantities of hydrochloric acid (Veley, *ibid.* 1908, 93, 652, 2114, 2122; 1909, 95, 758; Trans. Faraday Soc. 1908, 4, 19).

The degree of hydrolysis of a salt may also be measured with the aid of the hydrogen or quinhydrone electrode and plotting the  $pH$ -log. concentration) curve (V. Cupr, Z. anorg. Chem. 1931, 198, 310; Dupont, Compt. rend. 1931, 92, 1643; Kollhoff and Kameda, J. Amer. Chem. Soc. 1931, 53, 832), or with the glass electrode (Cranston and Brown, J. Roy. Tech. Coll. 1937, 4, 46; Trans. Faraday Soc., 1937, 33, 1455; J.C.S. 1940, 578).

The following percentage values have been obtained with 1.0-0.1M solutions (v. Cupr and Viktorin, A. 1931, 910).

Zinc sulphate . . .	0.0023-0.0046
Cadmium sulphate . . .	0.0006-0.0016

Beryllium halides and sulphate are also hydrolysed (M. Prytz, Z. anorg. Chem. 1929, 180, 355; 1931, 197, 103). The hydrolysis is regarded as of the type



as the values of  $K_0$  in the equation:

$$K_0 = A_H^2 \cdot C_{Be_2O^{++}} / [C_{Be^{++}}^2]$$

(where  $A_H$  represents the hydrogen ion activity) are practically constant and have the values  $K_0 < 10^7$ : sulphate 1.4, chloride 1.7, bromide 5.9 and iodide 4.4. In many cases rapid hydrolytic reactions are accompanied by secondary slow reactions in which the products of the primary hydrolysis coalesce to form products of high molecular weight and the application of the law of mass action is difficult if not impossible. The hydrolysis of salts of weak polybasic acids leads to isopoly acids which can exist in a narrow region of hydric concentration, whilst the hydrolysis of salts of weak poly-acid bases is characterised by isopoly bases which can exist in wide regions of hydric concentration (K. F. Jahr, A. 1938, 1, 202).

Most of the methods give only rough approximations (cf. Beveridge, Proc. Roy. Soc. Edin. 1909, 29, 648). A few of the results obtained are as follows:

Salt.	Temp.	% of salt hydrolysed in 0.1N solution.	Method.
Glycine hydrochloride	25	10.00	Hydrolysis of ester
Acetoxime "	25	36.00	" "
Urea "	25	90.00	" "
" "	60	81.00	Inversion of sugar
Sodium cyanide	25	1.10	Saponification of ester
" acetate	25	0.008	" "
" carbonate	25	8.17	" "
" phenate	25	3.05	" "
Aniline hydrochloride	60	2.60	Inversion of sugar
" "	25	1.50	Conductivity
Zinc chloride	100	0.10	Inversion of sugar
Aluminium chloride	100	6.10	" "
" "	25	0.50	Conductivity
Ferric chloride "	40	10.00	Inversion of sugar
Lead "	25	0.50	Conductivity

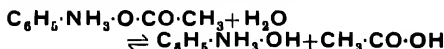
The whole question becomes more complicated when the acid or base formed by hydrolysis is unstable and is transformed into isomeric pseudo-acid or pseudo-base.

The influence of concentration on hydrolysis is given by Guldberg and Waage's law of mass action. According to this  $\frac{C_B}{C_A \times C_N} = \text{constant}$ , where  $C_B$  represents the concentration (molar) of the non-hydrolysed salt,  $C_A$  that of the acid formed by hydrolysis, and  $C_N$  that of the base. If originally 1 g.-mol. of salt was dissolved in  $v$  litres of solution and  $x$  g.-mols. were hydrolysed, then

$$1 - x / \frac{x}{v} = \text{constant, or } v(1-x) = \text{constant.}$$

It is obvious that as  $v$  increases, i.e. as the concentration is diminished,  $x$ , i.e. the degree of hydrolysis, must increase in order to keep the whole expression constant.

The relationships are not quite the same in the case of a salt derived from a feeble base and a feeble acid, e.g. aniline acetate,



If the reaction is represented as taking place between the ions of the salt and the water, and the salt is practically completely ionised, and the base and acid not appreciably, then  $C_{Cat} \cdot C_{An} / C_A \cdot C_N = \text{constant}$ , where  $C_{Cat}$  = concentration of the cation and  $C_{An}$  = concentration of the anion. But  $C_{Cat} = C_{An} = C_{Salt}$ .

$$\therefore C_{Salt}^2 / C_A \cdot C_N = \text{constant, or } \left( \frac{s}{v} \right)^2 \frac{a \cdot b}{v} = \text{constant}$$

where  $s$ ,  $a$ ,  $b$  are the gram-mols. respectively of salt, acid and base in  $v$  litres of solution. But this expression is independent of  $v$ , and hence dilution does not affect the degree of hydrolysis.

Another factor which affects the degree of hydrolysis is the addition to the solution of one of the products of hydrolysis, e.g. free acid or free base. Thus the hydrolysis of aniline hydrochloride in aqueous solution can be stopped completely by the addition of hydrochloric acid or of aniline. This follows again directly from the equation  $C_B / C_A \cdot C_N = \text{constant}$ . If  $C_A$ , i.e. the concentration of the acid, is increased it is necessary, in order that the whole expression may remain constant, that either  $C_B$  should diminish or  $C_N$  increase or both, and the only way in which this can be effected is by a diminution in the degree of hydrolysis.

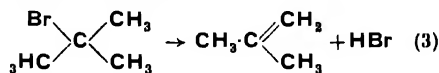
The velocity of salt hydrolysis has been determined in a few cases, e.g. ferric chloride (Goodwin, Z. physikal. Chem. 1896, 21, 1); potassium ruthenium chloride,  $K_2RuCl_6$  (Lind and Bliss, J. Amer. Chem. Soc. 1909, 31, 868).

A type of hydrolysis analogous to salt hydrolysis is that of the chlorides of certain non-metals, e.g.  $PCl_3 + 3H_2O = 3HCl + P(OH)_3$ . This reaction proceeds to completion in the presence of an excess of water, and, as a rule, the chlorides of non-metals are hydrolysed more readily than those of metals. Nitrogen trichloride and carbon tetrachloride are, however, stable in the presence of water and many

metallic chlorides derived from feebly electro-positive metals are appreciably hydrolysed, e.g.  $FeCl_3$ ,  $BiCl_3$ , etc.

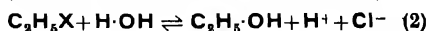
## II. HYDROLYSIS OF ORGANIC HALIDES.

A. Alkyl Halides.—A common method for the formation of alcohols is by the action of alkalis on alkyl halides, more particularly the bromides or iodides. With water alone an equilibrium is established  $RX + H_2O \rightleftharpoons R \cdot OH + HX$ . With many alkyl halides secondary reactions can occur, more particularly when the alkali is dissolved in aqueous alcohol. With ethyl halides and higher homologues there is always the possibility of the elimination of hydrogen halide and the formation of an olefin. This elimination is favoured when solvents rich in alcohol are used and moderately high temperature. It is essential that there should be a hydrogen atom in the position  $\alpha$ - to the halogen. In certain cases hydrogen halide can be eliminated and a cycloparaffin formed (*v. Cycloenes*). An accumulation of alkyl groups at the carbon atom to which the halogen is attached favours the formation of olefin, and elimination of hydrogen halide can occur in a solvent like anhydrous formic acid in the absence of alkali:



With concentrated ethyl alcoholic solutions of alkali the halogen is often replaced by the ethoxyl,  $-OEt$ , group, and the reaction is termed alcoholysis (*cf.* p. 397*b*). Equivalent quantities of different alkalis give different rates for the hydrolysis of ethyl chloride and follow the order  $\text{NaOH} > \text{Na}_2\text{CO}_3 > \text{CaO} > \text{MgO}$  (Izmalski and Papov, J. Gen. Chem. U.S.S.R. 1938, 8, 695).

Considerable attention has been given to the mechanism of this type of hydrolysis by Hughes, Ingold, Shapiro and their co-workers (J.C.S. 1935, 255; 1936, 225; 1937, 1177, 1183, 1187, 1192; 1938, 881; *cf. also* Taylor, *ibid.* 1935, 1514; 1937, 1962; 1938, 840, and reply to Taylor, *ibid.* 1940, 913, 920, 925, 935). The reaction between ethyl halides and water, acids or dilute alkali is one of the second order (Grant and Hunselwood, *ibid.* 1933, 258).



whereas with *tert*-butyl halides,  $\text{CMe}_3\text{X}$ , the reaction is one of the first order and can be represented as taking place in two stages (Hughes, *ibid.* 1935, 255):



The velocity actually measured by estimating  $\text{Cl}^-$  is that of the unimolecular reaction (a), i.e. the ionisation of the alkyl halide, as the second stage, (b), is very rapid.

The bimolecular reaction (2) is characteristic of most primary alcohols, but the accumulation of electron-releasing alkyl groups and still more of aryl groups at the seat of substitution of an alkyl halide causes the suppression of the reaction (2) and its replacement by reaction (1) involving

For the second-order reaction for ethyl and isopropyl bromides the values of  $k$  are roughly 25:1 and in the first-order reaction there is a marked increase from isopropyl to *tert*-butyl. The addition of water to the alcoholic solvent strongly accelerates the unimolecular reaction (1), slightly retards bimolecular substitution (2) and more strongly retards elimination. A comparison of the velocity coefficients of fluorides, chlorides, bromides and iodides of the same alkyl radical shows that there is a much greater difference between fluoride and chloride than between other pairs, *e.g.* for *tert*-butyl the ratios are: F:Cl 10<sup>5</sup>, Cl:Br=40, Br:I=2.5, and the same holds good for activation energies. The velocity coefficients (first order) for *tert*-butyl halides are some 10<sup>4</sup> times those for the corresponding isopropyl compounds. The proof that the hydrolysis of the *tert*-butyl compounds is of the unimolecular type,



is based on the following considerations.

(a) The rate constant for a given compound is the same in water, dilute acid or *very dilute* alkali. (b) By using a solvent with an ionising power towards alkyl halides as great as or greater than that of water, *e.g.* anhydrous formic acid, and adding small amounts of water, the *initial* velocity is found to be independent of the concentration of the water and the curves (time—Cl<sup>-</sup> concentration) are all the same in the early stages, but differ at later stages owing to the reversibility of the reaction. (c) By determining rates of both hydrolysis (replacement of Cl by OH) and alcoholysis (replacement of Cl by OEt) in the case of *tert*-butyl chloride it is found that the maximum rates of the two reactions have no connection with the composition of the product, whereas if the reaction were bimolecular the composition of the product could be calculated from the two rates (Olson and Halford, J. Amer. Chem. Soc. 1937, 59, 2644). For general discussion, see Bateman, Church, Hughes, Ingold and Taher (J.C.S. 1940, 979), and for hydrolyses in liquid sulphur dioxide, *cf.* Bateman, Hughes and Ingold (*ibid.*, 1011 and 1017).

Olefin is formed with anhydrous formic acid

OH for halide, Cowbray, Hughes, Ingold, Masterman and Scott (J.C.S. 1937, 1252) have drawn a number of conclusions relating to the Walden inversion. They conclude that bimolecular substitution leads to inversion and unimolecular leads normally to racemisation as the cation has a plane of symmetry, but that inversion can also occur if the life of the cation is very short. The reactions with silver oxide or silver salts are similar to unimolecular substitution. In each of the series:  $\beta$ -*n*-octyl,  $\alpha$ -phenylethyl,  $\alpha$ -substituted propionic acids,  $\alpha$ -substituted- $\alpha$ -phenyl- and  $\alpha$ -substituted- $\beta$ -phenyl-propionic acids, mono-substituted succinic acids the halogenated, hydroxy-, methoxy- and, in some cases, amino-compounds which have the same sign of rotation, *e.g.* +, have the same relative configurations, with the single exception of (+)  $\alpha$ -hydroxypropionic acid which has a configuration different from the (+) halogenated acids.

Based on these data conclusions are drawn with reference to the action of halides of phosphorus, thionyl chloride and hydrogen halides on hydroxy-compounds and the results confirm the views of Frankland (*ibid.* 1913, 103, 725) rather than those of Clough (*ibid.* 1918, 113, 526).

Olivier (Rec. trav. chim. 1934, 53, 869, 981), from a study of the reactions of the three chlorides  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ,  $\text{C}_6\text{H}_5\text{CHCl}_2$  and  $\text{C}_6\text{H}_5\text{CCl}_3$  and various substituted derivatives in aqueous acetone solutions of KOH and  $\text{H}_2\text{SO}_4$ , shows that the reactions are pseudo-unimolecular and in no case catalysed by hydrions. The hydrolysis of the first is catalysed by hydroxyl ions but that of the second and third is not, hence in the preparation of benzaldehyde from benzal chloride the addition of alkali is unnecessary. The effect of substituents in the phenyl group is such that the more negative the chlorine is rendered the less pronounced is the effect of hydroxyl ions. The hydrolysis of  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  in water is slower than in aqueous acetone, probably owing to the higher dielectric constant of water and hence the more negative character of the chlorine, *see also* Hackel, Annalen, 1939, 540, 274; and for effect of mercuric halides on hydrolysis of alkyl halides in aqueous acetone, *see* Read and Taylor, J.C.S. 1939, 1872; 1940, 679.



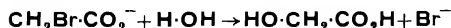
**B. Halogenated Fatty Acids and their Salts.**—Senter (J.C.S. 1907, 91, 460; 1909, 95, 1827; 1912, 101, 2528) has shown that hydrochloric acid or neutral salts have little or no effect on the hydrolysis of the free acids by water and that within wide limits the rate of hydrolysis is directly proportional to the concentration of the acid. At 102° the reaction is of the first order in dilute solutions, but deviations are met with in more concentrated solutions. With alkalis the reaction is of the second order in dilute solution. The hydrolysis with water is favoured by the introduction of alkyl groups into the molecule, whereas such groups retard the hydrolysis with alkalis.

Dawson and his co-workers (*ibid.* 1933, 49, 1133; 1934, 778; 1936, 153, 497) attribute the catalytic effect of acetate ions on the aqueous hydrolysis of sodium bromoacetate to the formation of an acetoxyacetate ion,

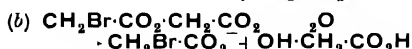
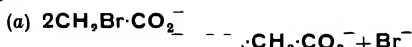


and in the absence of acetate ion the bromoacetate ion can catalyse by forming bromoacetoxyacetate ion,  $\text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2^-$ . The whole process comprises two distinct reactions:

(1) A reaction of the first order with excess water:



(2) A bimolecular reaction occurring in two stages:



and

$$v = v_1 + v_2 = k_1c + k_2c^2$$

where  $v_1$  and  $v_2$  are the velocities and  $k_1$  and  $k_2$  are the velocity coefficients of reactions (a) and (b) and  $c$  is the concentration of the  $\text{CH}_2\text{Br}\cdot\text{CO}_2^-$  cation.

In the presence of an added catalyst, *e.g.* acetate ion, formate ion or hydroxyl ion, the reaction can be represented as:

$$v = v_1 + v_2 + v_3 = k_1c + k_2c^2 + k_3c'$$

where  $c'$  is the concentration of the added catalyst and  $k_3$  the corresponding velocity coefficient. The most active catalyst is the hydroxyl ion and the fact that the course of alkaline hydrolysis can usually be expressed with close approximation to a simple bimolecular reaction is entirely due to the large value of  $k_3$  (for  $\text{OH}^-$ ) as compared with  $k_1$  and  $k_2$ .

With a mixture of free acid and sodium salt the reaction is more complex:

$$v = v_1 + v_2 + v_3 + v_4 \\ = k_1[\text{A}] + k_2[\text{A}]^2 + k_3[\text{HA}] + k_4[\text{HA}][\text{A}]$$

where  $[\text{A}]$  represents the concentration of the bromoacetate cation and  $[\text{HA}]$  the concentration of the un-ionised acid. The collisions between pairs of bromoacetic acid molecules have no measurable effect. By varying the conditions of the reaction any one of the four component reactions can be made the dominant factor in

the observed rate of change, and under certain conditions the general velocity equation reduces to very simple terms. The reaction becomes more complex when appreciable hydrolysis has taken place as the glycolate,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2^-$ , ions exert an influence and the whole velocity then becomes

$$v = k_1[\text{A}] + k_2[\text{A}]^2 + k_3[\text{HA}] + k_4[\text{HA}][\text{A}] \\ + k_5[\text{A}][\text{G}] + k_6[\text{HA}][\text{G}]$$

where  $[\text{G}]$  represents the concentration of the glycolate ions. The reactions between bromoacetic acid and hydrions, and collisions between pairs of bromoacetic acid molecules, glycolic acid molecules or bromoacetic acid and glycolic acid molecules have no measurable influence.

The relative values of  $k_1 \times 10^6$  to  $k_6 \times 10^6$  are: 0.059, 19.3, 0.041, 72, 35, 136. To render the results comparable all experiments were made with the same total salt concentration by the addition of sufficient sodium nitrate or sodium perchlorate.

The course of alkaline hydrolysis can be represented by the equation:

$$v = v_A + v_B + v_C + v_D \\ k_A[\text{A}][\text{OH}^-] + k_B[\text{A}][\text{H}_2\text{O}] + k_C[\text{A}]^2 + k_D[\text{A}][\text{G}]$$

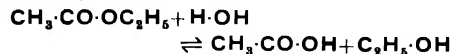
and as  $k_D$ ,  $k_C$  and  $k_D$  are all less than 0.01  $k_A$  it follows that the rate of alkaline hydrolysis is almost entirely dependent on  $k_A$ , so long as the concentration of  $\text{OH}^-$  is not too small. With very low  $\text{OH}^-$  concentrations the whole process cannot be represented as a simple bimolecular reaction.

### III. HYDROLYSIS OF ACYL DERIVATIVES.

Practically all acyl derivatives are hydrolysed more readily than the corresponding alkyl compounds; the esters and acid anhydrides more readily than the ethers; the acyl halides more readily than the alkyl halides; the amides, imides and anilides more readily than the stable amines.

**A. HYDROLYSIS OF ESTERS.**—The hydrolysis of an ester may be brought about by water alone, by solutions of neutral metallic salts, by aqueous solutions of strong alkalis or acids, by water in the presence of finely divided solids, such as charcoal, and also by means of enzymes.

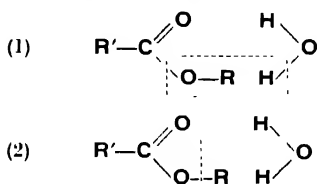
(1) **Hydrolysis with Water.**—The reaction with water may be represented by an equation of the type:



The reaction is the reverse of esterification, and is hence a balanced bimolecular reaction; in dilute solutions, however, the mass of the water may be regarded as remaining constant, and the reaction becomes practically non-reversible. Like esterification the reaction is slow and lends itself to study as a time reaction and also has a relatively high activation energy  $E$ . The course of the reaction can be followed by estimating the amount of free acid in the solution after given intervals of time; this is accomplished by removing an aliquot part of the solution at the given time and titrating the free acid by means of standard alkali solution. In most cases it is

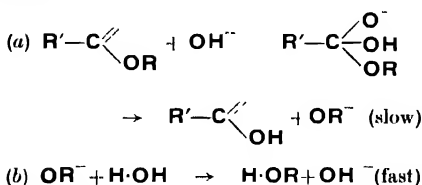
necessary to use a feeble alkali for titration, e.g. ammonium hydroxide with litmus as indicator, as nearly all esters which are hydrolysed appreciably by water are decomposed very readily by strong alkalis, and it becomes impossible to detect the end point of the titration when sodium or barium hydroxide solutions are used. Esters derived from comparatively strong acids, e.g. methyl sulphate, ethyl formate, ethyl trichloroacetate, ethyl pyruvate and ethyl tartrate are readily hydrolysed by water at room temperature. In these cases the velocity of the reaction does not correspond with that of a simple unimolecular reaction, the values for  $k$  calculated from the first order equation  $k = 1/t \log [a/a-x]$ , increase as  $t$  increases, and the probable reason is that the acid formed during the hydrolysis reacts catalytically on the reaction (see under hydrolysis by acids). Hydrolysis of natural glyceryl esters by means of superheated steam is used as a commercial method for the production of stearic acid for the manufacture of candles (v. this Vol., p. 45b).

**Mechanism of Hydrolysis.**—Two different types of fission of the ester molecule under the influence of water are possible :

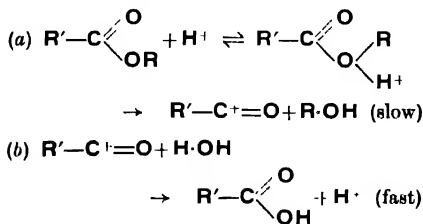


i.e. the fission occurs at the  $-\text{O}-\text{R}$  bond or at the  $\text{O}-\text{C}-\text{R}'$ , and all available evidence supports the former view, which was first suggested by Ferns and Lapworth (J.C.S. 1912, 101, 273).

Alkaline hydrolysis is represented by the scheme :

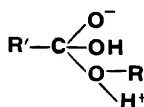


and acid hydrolysis by the scheme :



The two points of attack in the ester are the O of the OR group, which attracts protons, and the C of the CO group which attracts hydroxyl

ions. If both function then an ion common to both acid and alkaline hydrolysis would be formed :



The main arguments in favour of Ferns and Lapworth's view are : (a) An optically active ester containing a dissymmetric alkyl group gives, on hydrolysis—both acid and alkaline—the pure optically active alcohol (Holmberg, Ber. 1912, 45, 2997). If the hydrolysis followed scheme (2) the free alkyl radical would give a racemic alcohol. (b) When the ester contains an unstable unsaturated alkyl group, hydrolysis involving the elimination of R would bring about isomerisation and the alcohol formed would not correspond with the ester, e.g. the ester



yields the alcohol



and not the isomer :



or a mixture of the two (Ingold and Ingold, J.C.S. 1932, 758). (c) The strongest argument is the fact that when hydrolysis—either acid or alkaline—is carried out in the presence of water rich in heavy oxygen  $^{18}\text{O}$ , the alcohol formed contains no heavy oxygen and hence the O of the OR of the alcohol is derived from the ester and not from the water (Polanyi and Szabo, Trans. Faraday Soc. 1934, 30, 508; Datta, Day and Ingold, J.C.S. 1939, 838; Herbert and Blumenthal, Nature, 1939, 144, 248).

According to Kirmann (Bull. Soc. chim. 1934, [v], 1, 247) the hydrolysis of the four esters : (1) allyl pyruvate, (2) ethyl pyruvate, (3) allylidene acetate, (4) propylidene acetate, in water proceeds in two different ways : (a) a unimolecular spontaneous reaction (velocity coefficient  $k$ ), (b) a reaction with a velocity proportional to hydron concentration (proportionality constant  $b$ ). The values for  $k$  and  $b$  for the four esters at 25° and expressed in gram-molecules, litres and hours are : (1) 0.062, 8; (2) 0.025, 10; (3) 0.010, 8; (4) 0.004, 7. It is claimed that the results support Ferns and Lapworth's view of ester fission. In pure water the rate of hydrolysis of ethyl formate is proportional to hydron concentration and is retarded by addition of sodium formate. With ethyl acetate hydrolysis starts only after several days and is due to unknown impurities.

Experiments made with water and mixtures of water and deuterium oxide (Kailan and Ebender, Z. physikal. Chem. 1937, 190, 157, 1938, 182, 397), at 205° and in absence of a catalyst show that the  $\text{D}_2\text{O}$  retards the hydrolysis of methyl, *n*-propyl and *n*-butyl acetates and benzoates, but does not alter the equilibrium.

Kendal and Harrison (Trans. Faraday Soc. 1928, 24, 588) by an examination of freezing-point curves of mixtures of water with various

esters show that compound formation is common in all the systems examined, and that the tendency increases with the strength of the acid radical of the ester, whereas the nature of the alcohol radical appears to be of little influence in this respect.

For discussion on the evidence that hydrolysis is preceded by the addition of water to the O of the CO groups, *v. Adickes, Chem.-Ztg.* 1937, **61**, 167.

(2) **Acid Hydrolysis.**—The hydrolysis of esters by means of dilute mineral acids is slow and readily lends itself to study as a time reaction. The velocity is directly proportional to the concentration of the mineral acid, *i.e.* probably to that of the hydriions which act as a catalyst, and the reaction may be represented by the differential equation

$$dx/dt = k(c_{\text{ester}} \times c_{\text{H}_2\text{O}} \times c_{\text{H}^+})$$

In dilute solution (and most esters are somewhat sparingly soluble in water)  $c_{\text{H}_2\text{O}}$  can be regarded as not changing, and  $c_{\text{H}^+}$  is also constant, since the catalyst is not used up during the reaction. The process thus becomes a typical unimolecular reaction, and the velocity constant can be determined with the aid of the usual formula  $k = 1/t \log [a/(a-x)]$ .

The catalytic activity of the acid is not entirely due to the hydriions, but also to the un-ionised acid (*cf.* ESTERIFICATION). E. Ramstedt (*J.C.S.* 1915, **108**, ii, 541) gives the following formula:

$$v = k_1 \times C \times a + k_m \times C(1-a)$$

where  $v$  = rate of hydrolysis,  $k_1$  and  $k_m$  are coefficients characteristic of the hydriion and un-ionised acid respectively,  $C$  is the concentration of the acid, and  $a$  is the degree of ionisation. Experiments were made with ethyl acetate using various organic acids as catalysts, the degree of ionisation of the acids being determined by measurements of electrical conductivities of the free acids and sodium salts over a considerable range of dilution.

The concentration of the organic acid at any given time is obtained by titrating a portion of the solution with standard barium hydroxide solution and phenolphthalein (unless the ester is derived from a strong acid when ammonia and litmus are used) and subtracting from the total alkali used the amount required by the mineral acid. The following relative values have been obtained at 25°, with 0.1N-hydrochloric acid as catalyst acting upon the methyl, ethyl and propyl esters of acetic, propionic, butyric and valeric acids:

- $k$  methyl ester :  $k$  ethyl ester = 0.97
- and  $k$  ethyl ester :  $k$  propyl ester = 1.01
- $k$  acetate ester :  $k$  propionate ester = 1.07
- $k$  propionate ester :  $k$  butyrate ester = 1.75
- $k$  butyrate ester :  $k$  valerate ester = 2.93.

From these values it is clear that in the hydrolysis of an ester  $\text{R}'\text{CO}\cdot\text{OR}$  by means of a strong mineral acid the acyl group  $\text{R}'\text{CO}$  has a much greater influence than the alkyl group  $\text{R}$  on the velocity of hydrolysis (Hemptinne, *Z. physikal. Chem.* 1894, **13**, 562). Loewenherz (*ibid.* 1894, **15**, 389) working at a temperature

of 40° found that ethyl formate is hydrolysed much more readily than ethyl acetate (ratio 20:1); that methyl and ethyl monochloroacetates are hydrolysed at much the same rates, ratio 1.01:1; that the ratio ethyl acetate : ethyl monochloroacetate = 1.7; that ethyl dichloroacetate : ethyl monochloroacetate = 1.6; and that ethyl benzoate is hydrolysed extremely slowly.

Palomaa (*J.C.S.* 1914, **106**, i, 136) shows that with esters which contain an oxygen atom in the chain (whether as OH, OR, CO or O) the velocity of hydrolysis by mineral acids is reduced to a minimum when the oxygen atom is in the  $\beta$ -position with respect to the ester group. On the other hand, a cyano-group always has a retarding effect on the hydrolysis of an ester by dilute hydrochloric acid, and the effect is more pronounced in the  $\alpha$ - than in the  $\beta$ -position (*Amer. J. Sci.* 1914, [iv], **37**, 514). Drushel and Dean (*ibid.* 1912, [iv], **34**, 203) show that in the case of acetic acid the rate of hydrolysis is increased by the introduction of the hydroxy-group, but retarded by an alkoxy-group. The introduction of hydroxy-groups into the butyric acid, on the other hand, had a retarding effect (Dean, *ibid.* 1914, [iv], **37**, 331). For hydrolysis of halogenated esters, *see* Drushel, *ibid.* 1912, [iv], **34**, 69; for hydroxy- and alkoxy- derivatives of propionic acid, *ibid.* 1913, [iv], **35**, 486. As the result of experiments on the hydrolysis of the ethyl esters of propionic, acrylic, *n*-butyric, crotonic,  $\beta$ -phenylpropionic and cinnamic acids with dilute hydrochloric acid at 20°, Williams and Sudborough (*J.C.S.* 1912, **101**, 412) show that the rate of hydrolysis of the ethyl ester of an  $\alpha\beta$ -unsaturated compared with the rate for the corresponding saturated acid is about 1:30. The difference is however, not nearly so marked when an alkali (barium hydroxide) is used as hydrolysing agent.

Salmi (*Ber.* 1939, **72** [B], 1767) claims that most of the structural effects noted in the catalytic esterification of saturated and unsaturated fatty acids are also observed in the acid hydrolysis of the esters of these acids (*cf.* ESTERIFICATION).

The effect of olefin linkings in the alkyl group of an ester, as typified by the formates and acetates derived from allyl,  $\Delta^7$ -butenyl and  $\Delta^8$ -pentenyl alcohols, is only slight in the case of acid, but is somewhat more marked in alkali hydrolysis (Palomaa and Juvala, *Ber.* 1928, **61** [B], 1770).

Dawson and Lowson (*J.C.S.* 1928, 2146, 3218), by the elimination of autocatalytic effects on the hydrolysis of ethyl acetate by dilute hydrochloric acid and by determining the initial velocities, proved that, for concentrations of the hydrogen chloride between 0.0002 and 0.2 mol. per litre the initial velocity is proportional to the concentration of the acid. They claim that at all stages the velocity is determined by the hydrogen ion concentration of the solution. With concentrations of catalyst below 0.01 mol. the course of the hydrolysis is modified by the catalytic action due to the acetic acid produced. The relative importance of this autocatalytic effect increases as the con-

centration of the hydrogen chloride diminishes, and it is not possible in practice to determine the initial velocity of the reaction when the concentration falls below 0.0002 mol. per litre. By a careful study in silica vessels, as traces of alkali have a pronounced effect, it is shown that in moderately dilute solutions the reaction may be divided into two stages; in the first of these the velocity is determined by the joint catalytic activities of the  $H^+$  and  $OH^-$  ions, and in the second by the  $H^+$  ions only. It would appear that the speed of the uncatalysed reaction and the catalytic activity of the water molecules are too small to have any appreciable influence on the course of the reaction. Dilatometric study of the acid hydrolysis of ethyl orthoformate and acetol shows that hydrolysis other than by  $H^+$  ions is undetectable, and hence such a reaction is suitable for determination of hydrogen ion concentrations and for the investigation of the salt effect. In the case of all other ortho-esters, and of ketal, water molecules and substances like *m*- and *p*-nitrophenol, cacodylic and acetic acids produce catalytic effects in addition to the  $H^+$  ions.

For a résumé of evidence that catalytic effects are due to undissociated acid molecules as well as to  $H^+$  ions, see Bronsted and Wynne-Jones, *Trans. Faraday Soc.* 1929, **25**, 59. Working with a mixture of alcohol (42.34%) and water, Berger (*Rec. trav. chim.* 1924, **43**, 163) shows that the acceleration of the hydrolysis of esters with  $H^+$  ions decreases with the strength of the acid from which the ester is derived, and with methyl and ethyl esters of the same acid the difference in velocity is not constant, but decreases with the acidity of the ester. Olivier and Berger (*ibid.* 1927, **46**, 609, 861) show that hydrogen ion concentration is without effect on the hydrolysis of esters of strong acids or of compounds such as picryl acetate, and *s*-trinitrophenetole.

For effect of emulsifiers on hydrolysis, see Smith, J.C.S. 1925, **127**, 2602.

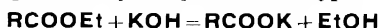
Strong organic acids such as trichloroacetic and picric, the  $HSO_4^-$  ion, and aqueous solutions of salts which give rise to hydrions act catalytically. Concentrated sulphuric acid at 15° rapidly hydrolyses ethyl phenylacetate and alkyl salicylates but only slowly ethyl phthalate and alkyl benzoates. At 80° the benzoates and phthalates are immediately hydrolysed and at the same time slowly sulphonated (Senderens, *Compt. rend.* 1904, **198**, 1827). An ester which is not hydrolysed by heating with strong hydrochloric acid or alkali, e.g. ethyl tetraethylsuccinate, can be hydrolysed by heating to 200° with hydrogen chloride and a little aluminum chloride, the products being ethyl chloride, water and the acid anhydride (Ott, *Ber.* 1937, **70** [B], 2362).

Practically all acid-catalysed reactions, including the inversion of sucrose and the hydrolysis of esters, proceed more quickly in heavy water,  $D_2O$ , than in water. This has been shown to be true of methyl acetate with sulphuric acid (Hornel, *Nature*, 1935, **135**, 909) and of ethyl formate and methyl acetate with hydrogen chloride (Butler and Nelson, J.C.S. 1938, 957), and in all such cases the complex of

the ester and hydron is in equilibrium with the medium (Bonhoeffer and Reitz, *Z. physikal. Chem.* 1937, **179**, 135; Wynne-Jones, *Chem. Reviews*, 1935, **17**, 115).

The mutarotation of *d*-glucose proceeds more slowly in  $D_2O$  than in water.

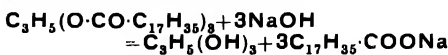
(3) **Alkaline Hydrolysis.**—The hydrolysis of an ester by means of an alkali hydroxide can be represented by an equation of the type:



The reaction is non-reversible, as the alkali salt cannot react directly with the alcohol, and as both ester and alkali are used up as the hydrolysis proceeds the reaction should be bimolecular. Hydrolysis by alkalis proceeds more rapidly than that by mineral acids (*cf.* Van Dijken, *Rec. trav. chim.* 1895, **14**, 106), and is the common method used in the laboratory. The ester is boiled for some time with an excess of sodium (or potassium) hydroxide solution in a reflux apparatus. If the ester is an oil only sparingly soluble in water, the completion of the reaction is denoted by the disappearance of the oily layer, unless the alcohol formed is also insoluble in water. If, however, the ester itself is soluble in water, the disappearance of its characteristic odour indicates complete hydrolysis. In order to separate the acid and alcohol formed, the mixture is (a) boiled, when the alcohol passes over together with water, provided the alcohol is a comparatively simple monohydric one; or (b) extracted with ether if the alcohol is complex and is not readily volatile. To obtain the acid the alkaline solute left after treatment (a) or (b) is acidified with hydrochloric acid, when the organic acid is directly precipitated if it is sparingly soluble in water, or can be extracted with ether if soluble in water.

An alcoholic solution of potassium hydroxide is sometimes used for hydrolysing purposes, especially when the ester is practically insoluble in water. In the case of esters other than ethyl, alcoholysis occurs resulting in the formation of ethyl esters which are then hydrolysed, e.g. glycol diacetate and alcoholic potash give ethyl acetate and glycol and finally ethyl alcohol, potassium acetate and glycol. Bryant and Smith (*J. Amer. Chem. Soc.* 1936, **58**, 1014) recommend heating the ester with excess of 2*N*-sodium hydroxide in 90% methyl alcohol at 60–100° in closed vessels.

The decomposition of esters by alkali hydroxide solutions is the basis for the usual methods for the manufacture of hard and soft soaps, and hence a common name for the process is *saponification*. The common fats are glyceryl esters of monobasic acids of high molecular weight, more especially of palmitic, stearic and oleic acids, and on saponification yield the trihydric alcohol glycerol and the sodium or potassium salts of the acids, e.g.



Anderson and Brown (*J. Physical Chem.* 1916, **20**, 195) have studied the velocity of saponification of various fats in different media; they find that the velocity is practically independent of the molecular weight of the fat but varies

considerably with the solvent and of the three alcohols used, namely, methyl, ethyl and amyl, is greatest in amyl alcohol.

The saponification of fat occurs in stages and if insufficient alkali is used, the product is a mixture of unaltered fat with mono- and diglycerides and free fatty acid (*cf.* Fortini, *Chem.-Ztg.* 1912, **36**, 1117; Marcusson, *Z. angew. Chem.* 1913, **26**, 173).

Reicher (*Annalen*, 1885, **228**, 257) was one of the first to determine the velocity of saponification under varying conditions. The reaction is a typical bimolecular one and the velocity coefficient can be calculated by means of the equation for a second order reaction:

$$k = \frac{1}{t(a-b)} \log_e \frac{b(a-x)}{a(b-x)}$$

where  $a$  and  $b$  are the original concentrations, and  $a-x$  and  $b-x$  the concentrations at the time  $t$ . The concentration of the alkali at any given time is determined by titration with standard acid and the concentration of the ester calculated from that of the alkali, as with an ester of the type of ethyl acetate, the disappearance of each gram-molecule of alkali entails the disappearance of a gram-molecule of ester (*cf.* Warder, *Amer. Chem. J.* 1882, **3**, 340; Ber. 1881, **14**, 1361). The velocity constant  $k$  can be calculated by means of the equation

$$k = \frac{1}{C_\alpha t} \log_e \frac{C_t(C - C_\alpha)}{C(C_t - C_\alpha)}$$

where  $C$ ,  $C_t$  and  $C_\alpha$  denote respectively the concentration of the alkali just after mixing, the concentration after time  $t$  and the concentration after complete hydrolysis (24-48 hours).

Reicher's experiments were carried out at 9.4°, and show that the velocity is practically the same whether sodium, potassium or calcium hydroxide is used as saponifying agent. With strontium or barium hydroxide the velocity constants are somewhat smaller and with a feeble alkali, such as ammonium hydroxide, the value for  $k$  is much less, *e.g.*

$$k_{\text{NaOH}} : k_{\text{NH}_4\text{OH}} = 200:1.$$

The addition of methyl alcohol, glycol, glycerol, dulcitol or mannitol in the alkaline hydrolysis of ethyl acetate reduces the rate and for di-, tri- and tetra-hydric alcohols the relationship  $k = k_0 G^{-c}$  holds good, where  $k$  is the velocity coefficient in a solution having a concentration of alcoholic hydroxyl groups equal to  $c$ ,  $k_0$  is the velocity coefficient in the aqueous solution and  $G$  is a constant (Sclivanova and Syrkin, *Compt. rend. acad. sci. U.R.S.S.* 1929, **23**, 45).

The results observed with different esters show that the alkyl group  $R$  in the ester



influences the rate of hydrolysis to a greater extent than it does when mineral acids are used for hydrolysing; thus the values for  $k$  using sodium hydroxide at 9.4° are: methyl acetate 3.49, ethyl acetate 2.31, propyl acetate 1.92, isobutyl acetate 1.62, and isooamyl acetate 1.64. The influence of the acyl group  $R'CO$

is also marked, as shown by the following values for  $k$  at 14.4°, using sodium hydroxide and ethyl esters: acetate 3.2, propionate 2.8, butyrate 1.7, isobutyrate 1.73, isovalerate 0.62, and benzoate 0.83.

Numerous investigations have shown that substituents introduced into the acyl group of an acid, whether aliphatic or aromatic, have a marked effect on the alkaline hydrolysis of its esters. In many cases this is a retarding effect, *e.g.* alkyl groups, especially in the  $\alpha$ -position in an aliphatic or in the  $o$ -position in a benzoic ester, generally retard hydrolysis (Hjelt, *Ber.* 1896, **29**, 1864; Gyr, *ibid.* 1908, **41**, 4308; Kellas, *Z. physikal. Chem.* 1897, **24**, 243). On the other hand certain substituents, *e.g.* chlorine in acetic acid (Sudborough and Feilman, *Proc. Chem. Soc.* 1897, **13**, 243),  $\alpha$ -hydroxyl in aliphatic acids (Findlay and Turner, *J.C.S.* 1905, **87**, 747; Findlay and Hickmans, *ibid.* 1909, **95**, 1004),  $o$ -halogen or nitro- in benzoic acid (Kellas, *loc. cit.*; Blakey, McCombie and Scarborough, *ibid.* 1926, 2863) increase the rate of alkaline hydrolysis. A comparison of the alkaline hydrolysis in 85% alcohol of the series of esters,  $R \cdot CO_2Et$ , where  $R$  increases from  $CH_3$  to  $n-C_7H_{15}$ , shows that the velocity coefficient decreases from  $CH_3$  to  $n-C_7H_{15}$ , and then remains almost constant. When  $R$  consists of a branching chain the constant falls and when  $R = CMe_3$  or  $CHEt_2$  the hydrolysis is remarkably slow. The change in velocity corresponds with a change in  $E$  in the Arrhenius equation with the exception of esters where the alkyl group branches at the  $\alpha$ -carbon atom. As a rule  $E$  varies with the inductive effect of  $R$ .

For the *ortho* effect in the hydrolysis of aromatic esters, see Kindler (*Annalen*, 1928, **464**, 278).

The generalisation drawn by V. Meyer (*Ber.* 1895, **28**, 1263; *cf.* Wegscheider, *ibid.* 1895, **28**, 2356), viz. that there is a simple relationship between the rate of hydrolysis of an ester by alkalis and its rate of formation by the catalytic method of esterification, does not hold. In a given series of esters the affinity constants of the acids from which the esters are derived and the saponification constants of the esters follow the same order, but there is no direct proportionality between the two sets of numbers.

Olsson (*Z. physikal. Chem.* 1928, **133**, 233) concludes that the velocity coefficient is mainly influenced by the strength of the acid component of the ester, but in certain cases steric influences affect the velocity in the opposite direction. It may be that the two influences are manifestations of one fundamental property, viz. the force of dissociation of the separate components (*cf.* Williams, Gabriel and Andrews, *J. Amer. Chem. Soc.* 1928, **50**, 1267). Smith and Olsson (*Z. physikal. Chem.* 1925, **118**, 99) point out that when the alkyl acetates are arranged in the order of decreasing rates of hydrolysis by sodium hydroxide the series is identical with the corresponding series for the rates of ester formation from the alcohols and acetic anhydride, and Olsson (*ibid.* 1927, **125**, 243), from a study of the rates of hydrolysis of numerous acetates by the same alkali, finds that branching in the alkyl radical, in contradistinction to simple lengthening of the carbon

chain, has a marked retarding effect on the rate. This conclusion is confirmed by Hol'tzschmidt, Vorob'ev and Potanov (J. Gen. Chem. U.S.S.R. 1936, 6, 757), who find that for a given acyl group the ratio  $k_{Et}/k_{Me}=0.57$ ,  $k_{Pr}/k_{Et}=0.84$  and  $k_{Bu}/k_{Pr}=0.93$ , but for a given alkyl group and different acyl groups the relationships are not so simple. The saponification of the ethyl esters of the saturated aliphatic acids has been studied by Evans, Gordon and Watson (J.C.S. 1938, 1439) to determine the effects of increasing  $R'$  from Me to *n*-butyl on P and E in the Arrhenius equation.

The alkaline hydrolysis of acetylated hydroxy-acids, e.g. acetylmandelic and acetylsalicylic acid, is bimolecular and free from side reactions, and a comparison of  $\alpha$ - and  $\beta$ -acetoxyphe-nyl-propionic acids shows that the ion of the  $\beta$ -compounds is hydrolysed more than twice as rapidly as the  $\alpha$ -ion (La Mer and Greenspan, J. Amer. Chem. Soc. 1934, 56, 1492). Also with unsaturated and phenyl substituted esters there is no parallelism between the rates of ester formation and the rates of saponification. The addition of an organic solvent to a mixture of methyl acetate, sodium hydroxide solution and alcohol tends to decrease the rate of hydrolysis (Caudri, Rec. trav. chim. 1929, 48, 422).

Kindler (Annalen, 1926, 450, 1; 1927, 452, 90) has examined the rate of hydrolysis of ethyl benzoate by a solution of sodium in 87-83% aqueous alcohol, and also of the esters with Cl, Br, I,  $NO_2$ ,  $CH_3$  and  $NH_2$  substituents, and finds that the rate increases in the order  $p-NO_2$ ,  $m-NO_2$ ,  $m-I$ ,  $p-I$ ,  $m-Br$ ,  $p-Br$ ,  $m-Cl$ ,  $p-Cl$ ,  $m-MeO$ ,  $p-Ph$ ,  $p-MeS$ ,  $m-Me$ ,  $p-Me$ ,  $p-Et$ ,  $p-MeO$ ,  $m-NH_2$ ,  $p-NH_2$ , or, generally, the reactivity decreases with the negativity of the group X in the complex  $XC_6H_4CO_2Et$ . When similar esters are examined, but with  $\cdot CH_2$ ,  $\cdot CH_2\cdot CH_2$  or  $\cdot CH\cdot CH$ , interposed between the nucleus and the carbethoxy group the substituents have similar effects and follow the same order, but the effect is most marked in the benzoic series, and least in the substituted phenylacetates.

The same author (Ber. 1936, 69 [B], 2702) attempts to correlate the rate of hydrolysis of an ester,  $RCO_2Et$ , with the firmness of the union between the R and carbethoxy-group.

Olivier and Weber (Rec. trav. chim. 1934, 53, 899), by a comparison of the ratio  $k_{OH}/k_H$ , i.e. the ratio of the velocity coefficients for the alkaline and acid hydrolysis of an ester, show that with different esters from the same alcohol the ratio increases with the strength of the acid from which the ester is derived.

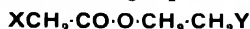
Ingold (J.C.S. 1930, 1032) claims that the ratio  $k_{OH}/k_H$  is free from all steric factors and represents only polar effects, and in a series of communications (Ingold and co-workers, *ibid.* 1930, 1039, 1375; 1931, 2035, 2043, 2170) the values for this ratio for different series of esters are given, calculated by a method based on Dawson's equation (*ibid.* 1926, 2872, 3166; 1927, 213, 1148, 1290)

$$2p_{H^+} - \log K_w = \log k_{OH}/k_H^1$$

<sup>1</sup> Where  $p_{H^+}$  is the  $p_H$  at which the velocity is at a minimum and  $K_w$  is the ionic product of water.

and thus involving the determination of the hydrolytic stability maxima of carboxylic esters. The ratio varies from 2 for ethyl acetate to 32 for ethyl chloroacetate, 160 for ethyl acetoacetate and 12,000 for ethyl aminoacetate.

The results for the two groups of esters:



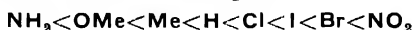
and



where X and Y represent substituents, show that the ratio increases regularly with the electron-attracting nature of X, e.g. from H through Cl,  $CH_3\cdot CO$  to  $NH_3^+$ , but decreases with the electron-donating value of X, and similar generalisations hold good for the substituent Y.

Three general conclusions are drawn: (1) that two methyl groups in the same position relatively to  $\cdot COO\cdot$  in  $R\cdot COOR'$  displace  $p_H$  by roughly equal amounts; (2) that the displacement of  $p_H$  by the introduction of a methyl or *gem* dimethyl group decreases approximately geometrically as successive carbon atoms are included normally between the group and the  $\cdot COO\cdot$  nucleus; (3) that the displacement of the minimum caused by any group in  $R'$  bears a nearly constant ratio to the displacement produced by the same group in R. It is further concluded that the same quantitative measure of polarity may be derived from other chemical reactions.

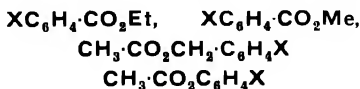
Conclusions on the relationship between polar effect and energies of activation (E) in processes of hydrolysis have been drawn by several investigators. Ingold and Nathan (*ibid.* 1936, 222) have examined the alkaline hydrolysis of *p*-substituted benzoic esters from the point of view of the Arrhenius equation  $k = Be^{-E/RT}$  in 85% aqueous alcohol at 25° and 50°; B is the reaction constant which depends primarily upon the frequency of collision of the reacting molecules (Moelwyn-Hughes, "Physical Chemistry," 1940, p. 532);  $k$  varies with the substituent in the following order:



over a 5,000 fold range and the activation energy decreases in the order:



and the linear relationship between E and  $\log k$  corresponds with a constant value of B in the equation. Timms and Hinshelwood (*ibid.* 1938, 862), from a study of both acid and alkaline hydrolysis in aqueous acetone and aqueous alcohol, show that the reaction is facilitated by recession of electrons from the seat of the reaction. The value of E is high in acid hydrolysis and the effects of substituents are smaller; also B increases with E in contrast with the constant value in alkaline hydrolysis. The effect of the solvent is apparently the opposite in the two cases. The effects of the transmission of substituent influences have been studied by Newling and Hinshelwood (*ibid.* 1936, 1357) and Tommila and Hinshelwood (*ibid.* 1938, 1801). The esters examined belonged to the series:



and

where  $X$  is in the  $m$ - or  $p$ -position. In all cases of alkaline hydrolysis  $B$  remains constant and changes due to the substituent are measured in change in  $E$ . In acid hydrolysis the change is similar but less regular. In the former case the value  $\Delta E^1$  gives a qualitative measurement of the influence of the different substituents for a given series, and the values are fairly constant for all the series. The changes in  $E$  are a measure of the transmission of the electronic effect of a given substituent through the given structures.

The same set of substituents does not produce equal effects in different reactions, but if  $\Delta E_1$  is the change caused by any given substituent in one reaction and  $\Delta E_2$  that caused by the same substituent in a second reaction then  $\Delta E_1 = a\Delta E_2$  where  $a$  is practically constant for all the substituents. The transmission coefficient for the influence of the substituent to the reaction centre is greatest in the case of the alkaline hydrolysis of benzoic esters and decreases in the order phenyl acetates (alkaline) (0.71), benzyl acetates (alkaline) (0.36), benzoic esters (acid) (0.2), phenyl acetates (acid) and benzyl acetates (acid). The numbers in brackets give the relative values.

Ingold and his co-workers (*ibid.* 1931, 2035) from the values of  $k_H$  at different temperatures have calculated the values of  $A$  and  $B$  in the equation

$$\log_{10} k_H = A - B/T.$$

Although the values of  $k$  do not fall regularly but exhibit a maximum with the propionyl radical, neither  $A$  nor  $B$  exhibits this anomaly; both  $A$  and  $B$  fall as the length of the acyl group increases from acetyl to pentoyl.  $A$  is primarily a steric function and  $B$  a polar function.

The activation energies and velocities of acid and alkaline hydrolysis of trilaurin, tripalmitin, tristearin,  $\alpha\alpha$ -dipalmitin and  $\alpha$ -monopalmitin in the expanded state in monolayers approximate to those in homogeneous solution and on compression to the condensed state the values of  $E$  rise although those of  $k$  change only slowly (Alexander and Rideal, *Proc. Roy. Soc.* 1937, A, 163, 70).

The activation energies for alkaline saponification of substituted aromatic esters can be correlated with the dipole moments ( $\mu$ ) of the substituent groups according to the equation  $E = E_H + a\mu + b\mu^2$ , where  $a$  and  $b$  are constants (Nathan and Watson, *J.C.S.* 1933, 1249).

(4) **Finely Divided Metals, Metallic Oxides and Salts as Catalysts.**—Esters can also be hydrolysed by water with finely divided metals as catalysts, e.g. Neilson (*Amer. J. Physiol.* 1903, 10, 191) has shown that platinum black accelerates the hydrolysis of ethyl butyrate. The reaction is, however, very slow, and increases with the amount of platinum present. The maximum effect is obtained at 50°, and the activity of the catalyst is readily destroyed by various "poisons." The reaction is reversible as platinum black can also accelerate the esterification of butyric acid in ethyl alcoholic solution.

Sabatier and Maible (*Compt. rend.* 1911, 152,

494) have shown that titanium dioxide is a good catalyst for the conversion of acids and alcohols into esters. The method adopted is to allow a mixture of molecular quantities of the vapours of the two compounds to pass over a column of the dioxide kept at 280–300°. The yield of ester is much the same as in Berthelot and Menschutkin's experiments, but the process is extremely rapid. The reaction is reversible, and using equivalent quantities of acid and alcohol an approximately 70% yield of ester was obtained in most cases examined. A similar method may also be used for hydrolysis of esters. It consists in allowing a mixture of the vapour of the ester with an excess of steam to pass over the titanium dioxide at 280°–300°.

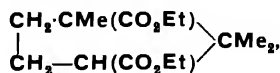
Similar results can be obtained with thorium oxide as catalyst provided aromatic acids of the type of benzoic are used (*ibid.* 1911, 152, 358).

Certain neutral metallic salts also act catalytically on the hydrolysis of esters by water (Kellog, *J. Amer. Chem. Soc.* 1909, 31, 403, 886). The salts which have been investigated are potassium chloride, bromide and iodide. The catalytic effects are comparatively small when compared with those of strong acids; the chloride has the greatest effect and the iodide the least, and when the concentration of the salt reaches a certain value the catalytic effect is negative.

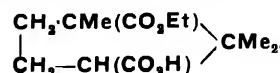
Holmes and H. C. Jones (*J. Amer. Chem. Soc.* 1916, 38, 105), working with aqueous solution of methyl acetate and methyl formate, show that salts with water of crystallisation have a greater effect in increasing the velocity of hydrolysis than anhydrous crystalline salts. Certain salts such as  $\text{Li}_2\text{SO}_4$ ,  $\text{NaI}$ ,  $\text{SrBr}_2$ ,  $\text{LiBr}$  and  $\text{KI}$  produce retarding effects. On dilution the effect with salts having water of crystallisation decreases more rapidly than with crystalline anhydrous salts, and this shows that the decomposition of the esters cannot be due to the hydrolysis of the salts alone.

(5) **Esters of Dibasic Acids.**—J. Meyer (*Z. physikal. Chem.* 1909, 66, 81; 67, 257) by the study of the hydrolysis of esters of dibasic acids (tartaric, succinic and camphoric) with hydrochloric acid as catalyst, has proved that the reaction proceeds in two distinct stages: (a) normal ester + water  $\rightarrow$  acid ester + alcohol; (b) acid ester + water  $\rightarrow$  acid + alcohol. With the ethyl esters of symmetrical dibasic acids, e.g. tartaric and succinic, the whole reaction appears to be unimolecular as the velocity constant for the first stage is almost exactly double that for the second stage, and the whole is pseudo-unimolecular. This simple relationship does not hold good for oxalic acid or unsaturated acids, e.g. maleic.

In the case of ethyl camphorate, the ester of an unsymmetrical acid, the two stages proceed at very different rates; the normal ester,



is rapidly hydrolysed to the  $\beta$ -acid ester,

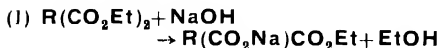


<sup>1</sup>  $\Delta E = E_H - E_X$ , where  $E_H$  is the energy of activation of the unsubstituted acid and  $E_X$  that of the substituted acid.

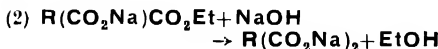
but this latter is fairly stable, and the method is a convenient one for the preparation of the acid ester. For different esters of the same acid the influence of the alcoholic group on the rate of hydrolysis is scarcely noticeable, whereas the constitution of the acyl group has a marked effect.

Experiments carried out with the same esters using alkali hydroxide as hydrolysing agent show that here also the reaction proceeds in two distinct stages, but the relationship between the velocity constants of the two is not so simple as when hydrochloric acid is used.

The two stages are—



and



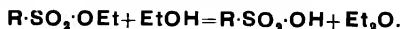
and their respective velocity coefficients are denoted by  $k_1$  and  $k_2$ . Ritchie (J.C.S. 1931, 3112) has developed an accurate method for determining  $k_1$ ; and  $k_2$  can be readily determined by employing the sodium salt of the monoethyl ester, and using the usual bimolecular formula for calculation, whereas Nielsen (J. Amer. Chem. Soc. 1936, 58, 206) has used a conductivity method. Addition of ethyl alcohol diminishes very considerably the rate of the reaction in aqueous solution. The ratio decreases in all cases as the proportion of alcohol in the mixture is increased.

With ethyl oxalate the ratio  $k_1/k_2$  is 10<sup>4</sup>, with ethyl malonate 100, ethyl succinate 10 and ethyl sebacate 2.8 (Ingold, J.C.S. 1930, 1375; 1931, 2170), and the whole process cannot be represented as a simple bimolecular reaction. The values have been used for calculating  $r$ , the distance in cm. between the carboxylic groups and  $r \times 10^8$  varies from 2.9 for oxalic to 12.38 for azelaic. With the esters derived from symmetrical dihydric alcohols, e.g. glycol diacetate,  $\text{C}_2\text{H}_4(\text{OAc})_2$ , although the hydrolysis proceeds in two distinct stages the velocity constants of the two stages bear a simple relationship to one another, e.g. 2:1, and hence the whole appears to be a bimolecular reaction. The same holds good for the hydrolysis of glyceryl triacetate, where the three distinct stages proceed at the relative rates 3:2:2.

Measurements of the velocity of hydrolysis by potassium hydroxide in mixtures of alcohol and water show that the velocity coefficient is not a continuous function of the composition of the solvent. At 15° the discontinuities in the plotted curves correspond closely with simple molar ratios of alcohol and water, and at higher temperatures the number of such discontinuities is small. Similar results are not met with in other reactions studied in alcohol-water mixtures (McCombie, Scarborough and Settle, *ibid.* 1921, 119, 970; 1922, 121, 243, 2308). The values of  $k_1$  and  $k_2$  and also the ratio  $k_1/k_2$  diminish as the percentage of alcohol increases (Ritchie, *ibid.* 1931, 3112).

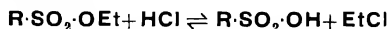
(6) **Esters of Sulphonic Acids.**—Esters of sulphonic acids are also hydrolysed by water, mineral acids or alkalis, and since most of the

sulphonic acids are very strong acids, their esters are hydrolysed quite readily by water alone. The esters are also converted into the corresponding acids when heated with alcohol (Krafft and Roos, Ber. 1893, 26, 2823; Kastle and Murrill, Amer. Chem. J. 1895, 17, 290), a reaction in which an alkyl ether is also formed



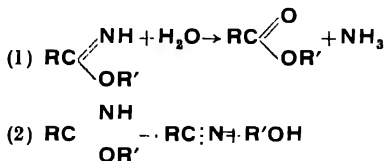
This decomposition proceeds slowly at the ordinary temperature, and is brought about more readily by methyl than by ethyl alcohol.

Kastle, Murrill and Frazer (*ibid.* 1897, 19, 894) have shown that 0.1*N*-solutions of sulphuric and acetic acids have no effect on the hydrolysis of esters of sulphonic acids by water. Hydrochloric and hydrobromic acids, on the other hand, have an apparent retarding effect, but this is due to the fact that the halogen hydrides can react with the ester according to the equation:



a reaction which does not affect the total acidity of the solution. A more detailed investigation has proved that this second reaction proceeds more rapidly and to a greater extent than the hydrolysis of the ester by water. The hydrolysis of a sulphonic ester by means of a large excess of water or alcohol in acetone solution gives concordant values for  $k$  when the equation for a unimolecular reaction is used. Alkalis are much more efficient hydrolysing agents than water for sulphonic esters; this may be due to the alkali acting independently of the water or to the alkali catalytically affecting the hydrolysis by water. The constants at 25° for methyl benzenesulphonate, using water and *N*-potassium hydroxide solution are in the ratio 1:90 (Wegscheider and Furcht, Monatsh. 1902, 23, 1903). When the neutral ester of a mixed carboxylic sulphonic acid is hydrolysed, e.g.  $\text{EtO}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ , the  $\text{SO}_2\cdot\text{OEt}$  group is hydrolysed much more readily than the  $\text{CO}_2\text{Et}$  group, and an acid ester of the type  $\text{HO}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$  is formed.

(7) **Imino-ethers** can be hydrolysed in two different ways:



The former reaction is greatly accelerated by acids and the latter by alkalis. According to Stieglitz (Amer. Chem. J. 1908, 39, 29, 166) the former reaction consists in the hydrolysis of the complex cation  $(\text{RC}:(\text{NH})\text{OR}', \text{H}^+)$ , and the latter in the decomposition of the anion

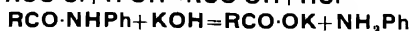
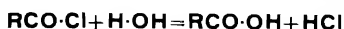


The effect of alkalis is much more pronounced than that of acids. When water alone is used it is the non-ionised ether which is decomposed.

**B. HYDROLYSIS OF OTHER ACYL DERIVATIVES.**—The chlorides, amides, anilides and



anhydrides of organic acids can be hydrolysed in much the same manner as esters, *e.g.*



**Amides.**—As a rule the derivatives of aliphatic acids are hydrolysed more readily than those derived from aromatic acids, *e.g.* acetamide more readily than benzamide. The hydrolysis is usually effected by boiling with alkali hydroxide, but the presence of *ortho*-substituents in derivatives of benzoic acid retards hydrolysis to an appreciable extent (V. Meyer, *Ber.* 1894, **27**, 2153; Sudborough, *J.C.S.* 1894, **65**, 1030, 1895, **67**, 587; 1897, **71**, 229; Reed, *Amer. Chem. J.* 1899, **21**, 281). When two such substituents are present the amide cannot be hydrolysed by boiling with potassium hydroxide solution, but the hydrolysis may be accomplished by heating with concentrated hydrochloric or hydrobromic acid under pressure in sealed tubes. One of the most convenient methods for converting a di*ortho*-substituted benzonitrile into the corresponding acid is to hydrolyse to the amide  $\text{RCN} + \text{H}_2\text{O} = \text{RCONH}_2$  by heating at 120–130° with 90% sulphuric acid, and when cold to replace the amino group by hydroxyl by the addition of sodium nitrite solution (Bouveault, *Bull. Soc. chim.* 1892, [iii] **9**, 368; Sudborough, *J.C.S.* 1895, **67**, 602).

An  $\alpha\beta$ -olefin linking in the acyl group has a retarding effect on the hydrolysis of an acid amide with sulphuric acid or alkali (Yathraja and Sudborough, *J. Indian Inst. Sci.* 1925, 55).

The hydrolysis of acetamide by hydrochloric acid has been studied by Acree and Nirdlinger (*Amer. Chem. J.* 1907, **38**, 489). The amount of hydrolysis after given intervals of time was determined by introducing known volumes of the reaction mixture into a Lunge nitrometer containing sodium hypobromite solution and measuring the nitrogen evolved. Their results show that at 65° the reaction is practically unimolecular when dilute solutions are used, but that the values for *k* tend to increase with the time, probably owing to a slight catalytic effect of the ammonium chloride formed on hydrolysis.

The mechanism of the reaction is probably analogous to that of the acid hydrolysis of esters, the first stage being the formation of a cation  $\text{RCO}\cdot\text{NH}_2\text{H}^+$  from the amide and hydron and the second stage the reaction of this cation with water yielding the organic acid and the ammonium ion.

Crocker and Lowe (*J.C.S.* 1907, **91**, 593, 952) have studied the hydrolysis of the amides of the simple aliphatic acids with hydrochloric acid, and also with sodium hydroxide solution, using the electrical conductivity method in order to determine the amount of amide hydrolysed. The order of the amides when hydrochloric acid is used is formamide, propionamide, acetamide, isobutyramide, capronamide, butyramide and valeramide; but with sodium hydroxide the order is formamide, acetamide, propionamide, capronamide, butyramide, isobutyramide and valeramide; in both cases formamide is the amide most readily hydrolysed, and in every case the hydrolysis with alkali proceeds more rapidly

than that with hydrochloric acid under similar conditions.

Most compounds of the type of alkylated acid amides, *e.g.* compounds containing the grouping  $\text{R}\cdot\text{CONHR}$ , can be hydrolysed. Thus hippuric acid (benzoylglycine),

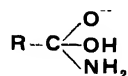


is hydrolysed to benzoic acid and glycine hydrochloride when boiled with concentrated hydrochloric acid. For alkaline hydrolysis of compounds of the type  $\text{CCl}_2(\text{CONHR})_2$ , where  $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{Me}$ ,  $\text{C}_6\text{H}_4\text{Cl}$ ,  $\text{C}_7\text{H}_{15}$ ,  $\text{CH}_2\text{Ph}$ , see Naik, Trivedi and Mehta, *J. Indian Chem. Soc.* 1938, **15**, 426.

**Nitriles.**—The hydrolysis of an aliphatic nitrile by either acids or alkalis occurs in two distinct stages, the intermediate product being the acid amide. The first reaction takes place much more slowly than the second, and is the one actually measured when hydrochloric acid is used as catalyst (Kilpi, *Z. physikal. Chem.* 1914, **86**, 641; for alkaline hydrolysis *cf. ibid.* p. 740).

E. Fischer (*Ber.* 1898, **31**, 3266) has pointed out that uric acid and similar cyclic nitrogen derivatives are less readily hydrolysed by dilute alkalis than their alkylated derivatives, *e.g.* 1:3:9-trimethyluric acid. Similarly the amide and methyl ester of the methyl ether of salicylic acid are more readily hydrolysed than the corresponding derivatives of salicylic acid itself, and in all such cases the compounds most resistant to the hydrolysing agent are those which can form metallic salts with the alkalis.

The hydrolysis is analogous to the alkaline hydrolysis of esters, the complex anion



being the first product and the second stage the decomposition of this into ammonia and the anion of the organic acid. When the amide contains a replaceable hydrogen atom, salt formation of a different type occurs, and the characteristic complex anion is not formed.

**Lactones and Anhydrides of Dibasic Acids.**—In the hydrolysis of both types of compounds water is added but no fission occurs; the first group gives the hydroxy-acids and the second the dibasic acids.

The relative rates of hydrolysis of lactones have been used by Haworth and Nicholson (*J.C.S.* 1926, 1899) to determine whether a lactone derived from the sugar acids is a  $\gamma$ - or  $\delta$ -lactone, as the former is hydrated much more slowly than the latter.

For the ketonic and acid hydrolyses of substituted ethyl acetoacetates and their utilisation in the preparation of substituted acetones and acetic acids, see ACETOACETIC ACID, and for hydrolysis of aromatic sulphonic acids by mineral acids, where *o*- or *p*-methyl groups facilitate and *o*- or *p*-amino groups retard hydrolysis, see Crafts, *Bull. Soc. chim.* 1907, [iv], 1, 917.

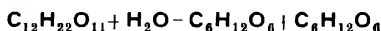
#### IV. HYDROLYSIS OF GLYCOSIDES, DI- AND POLY-SACCHARIDES.

As a rule compounds of the ether type, i.e. compounds containing two alkyl or substituted alkyl groups attached to oxygen, are not readily hydrolysed when boiled with alkali or acid solutions.

All the carbohydrates of the di- or polysaccharide type take up water when warmed with dilute mineral acid and are resolved into monosaccharides. The best known examples are:

Sucrose (cane sugar) + water  
                                   glucose (dextrose) + fructose (levulose)  
 Malt sugar + water    glucose  
 Lactose (milk sugar) + water = glucose + galactose.

All these reactions can be represented by the equation:



Starch is also hydrolysed by dilute mineral acids yielding as final product glucose:



The hydrolysis of cane sugar (sucrose) by means of dilute mineral acid has been examined in detail; it is usually referred to as the inversion of sucrose, as the optical rotatory power changes from + to - during the reaction. The investigations of Wilhelmy (Pogg. Ann. 1850, **81**, 413, 499) proved that in dilute solution the amount of sugar inverted is proportional to the amount present, or, in other words, the reaction is unimolecular. The method of determining the concentration of the sucrose at any given time is based on polarimetric readings. If the original rotation of the sucrose solution be  $+x^\circ$ , and after complete inversion be  $-y^\circ$ , then the total change is  $x^\circ + y^\circ$ . If after an interval of time  $t$  the rotatory power of the solution is  $+z^\circ$ , then the fraction of sucrose which has

undergone inversion is  $\frac{x-z}{x+y}$ , and the velocity constant can be determined by substituting the values for  $t$ ,  $C_0$ , and  $C_t$  in the equation

$$K = 1/t \log_e (C_0/C_t)$$

where  $C_0$  represents the concentration of the sucrose at the beginning, and can be expressed by  $x+y$ ,  $C_t$  represents the concentration at time  $t$ , and is equal to  $x-z$ . The velocity of inversion is directly proportional to the concentration of the hydrochloric acid, and increases with rise in temperature (J. Meyer, Z. physikal. Chem. 1908, **62**, 59; Hudson, J. Amer. Chem. Soc. 1908, **30**, 1165; Rosanoff, Clark and Sibley, *ibid.* 1911, **33**, 1911).

The dilatometric method has been used for determining the rate of hydrolysis of sucrose with dilute hydrochloric acid and the results follow the unimolecular formula (Hitchcock and Dougan, J. Physical Chem. 1935, **39**, 1177) and the velocity coefficients agree with those determined polarimetrically. The total contraction per gram-molecule at infinite dilution is 6.92 c.c. at 25° when the products are in mutarotation equilibrium.

The hydrolysis of other disaccharides, and

of glycosides by dilute mineral acids also follows Wilhelmy's Law, but the relative rates are very different; the following values have been obtained for *N*-sulphuric acid at 20°: lactose 1, maltose 1.27, sucrose 1240; also  $\alpha$ -methylglucoside 100, and  $\beta$ -methylglucoside 179. The hydrolysis of carbohydrates by means of dilute mineral acids is the basis of certain commercial methods for the manufacture of glucose. Large quantities of this carbohydrate are manufactured by boiling starch (e.g. potato or maize starch) with dilute sulphuric acid, removing the acid by precipitating as calcium sulphate and evaporating the clear solution under reduced pressure. Hydrochloric acid is used in U.S.A. and wood cellulose is hydrolysed by concentrated hydrochloric acid in Germany, and the resulting glucose fermented for the production of power alcohol.

All glycosides, including the simple synthetic alkylglucosides and all the more complex natural glycosides (v. GLYCOSIDES), are readily hydrolysed by dilute acids or alkalis. In these compounds the alkoxyl- or more complex radical is attached to the first carbon atom of the aldose molecule, i.e. the carbon atom of the group with aldehydic functions in aqueous solution. The primary product is the corresponding  $\alpha$ - or  $\beta$ -form of the aldose, but as these rapidly undergo mutarotation in the presence of acid or alkali the final product is a solution of the  $\alpha$ - and  $\beta$ -forms in equilibrium. Other methyl derivatives, e.g. those with OMe in positions 2, 3, 4 or 6 of a pyranose, are not readily hydrolysed and behave as ordinary ethers.

Ultra-violet light can bring about the hydrolysis of glycosides, also of certain esters and amides, but not of polypeptides or proteins (Guillaume and Tanret, Compt. rend. 1935, **201**, 1057).

From determinations of the velocity coefficients for hydrolysis of certain fructo-furanosides and -pyranosides at 20–60° Heidt and Purves (J. Amer. Chem. Soc. 1938, **60**, 1200) prove that the generalisation  $\log k = \log a - b/T$  holds good, and that  $\log a$ ,  $b$  and  $E$  (activation energy) increase when methyl replaces benzyl, when an  $\alpha$ - replaces a  $\beta$ -isomeride and when a pyranoside replaces a furanoside.

*Neutral Salt Action.*—The investigations of Ostwald (J. pr. Chem. 1883, [ii], **28**, 460), Spohr (*ibid.* 1886, [ii], **33**, 265), and Arrhenius (Z. physikal. Chem. 1889, **4**, 234; 1899, **31**, 207) prove that the addition of a substance which is largely ionised in aqueous solution accelerates the hydrolysis of esters or of carbohydrates by aqueous solutions of strong acids. This has been proved by the addition of metallic chlorides to mixtures in which hydrogen chloride is the catalyst, the addition of bromides to hydrogen bromide, and of nitrates to nitric acid. The majority of chlorides have much the same effect if readily ionised, whereas a salt such as mercuric chloride, which is only partly ionised, has a much feebler action.

Caldwell (Proc. Roy. Soc. 1906, A, **78**, 272), working with weight-normal solutions, shows that the presence of metallic chlorides increases the catalytic activity of hydrogen chloride in

the inversion of cane sugar, and that calcium chloride has the most pronounced effect. Similar effects on the activity of nitric acid are produced by nitrates (Whymer, *ibid.* 1907, A, 79, 576). Salts also tend to increase the activity of hydrogen chloride when used as a catalyst in the hydrolysis of methyl acetate (Armstrong and Watson, *ibid.* 1907, A, 79, 579), but their effect is not so marked as in the case of the inversion of sucrose (*cf.* Armstrong, *ibid.* 1908, A, 81, 90; Armstrong and Crothers, *ibid.* p. 102). Senter (J.C.S. 1907, 91, 462) states that in equivalent solutions of different salts the effect is practically independent of the nature of the salt (*cf.* Jones, Z. physikal. Chem. 1906, 55, 355, 429). Change of temperature has but little effect on neutral salt action, and it is concluded that probably the earlier suggestion of Arrhenius is correct, namely, that the ions of the neutral salt have some action on the hydrions or hydroxyl ions of the catalyst.

Reed (Amer. Chem. J. 1899, 21, 342) states that neutral salts retard the hydrolysis of acid amides by alkalis; and Arrhenius (Z. physikal. Chem. 1887, 1, 110) and Spohr (*ibid.* 1888, 2, 1194) claim that the same effect is produced by salts on the rate of hydrolysis of esters by alkalis. For the action of neutral salts on hydrolysis of chloroacetic acid, *cf.* Section III B, p. 385a.

#### V. HYDROLYSIS BY ENZYMES.

Many of the hydrolytic processes induced by aqueous solutions of acids or alkalis can also be brought about by the complex organic substances found in animal and plant tissues known as enzymes. For chemical nature of enzymes, purification, factors influencing enzyme action and kinetics of enzyme action, *see* ENZYMES.

The name given to a particular hydrolysing enzyme usually indicates the substance it is capable of hydrolysing and in these cases the termination *ase* is used. Thus maltase is the enzyme which hydrolyses maltose, amylase the enzyme which hydrolyses starch; but in some cases older names which were in use before this scheme was adopted, are still retained, *e.g.* sucrase, the enzyme which inverts sucrose (cane sugar), is still called invertase or even invertin, the common digestive enzymes are termed trypsin and pepsin. The substance which is decomposed by the enzyme is usually termed the substrate.

The more important types of hydrolysing enzymes are:

- (I) Ester- and fat-splitting enzymes—lipases and esterases.
- (II) Carbohydrate- and glycoside-splitting enzymes. Invertase or sucrase, maltase, amylases and the naturally occurring glycoside-splitting enzymes, *e.g.* amygdalin, myrosin, etc.
- (III) Proteolytic enzymes which hydrolyse proteins and polypeptides (for list, *see* ENZYMES).

All three groups are of great interest as they play an important part in the digestion and assimilation of food. Many are also of value

in industry, *e.g.* in the malting of barley where the invertase or amylase breaks down the starch through dextrins and maltose to glucose.

As catalysts they differ in several respects from the general hydrolytic catalysts, mineral acids and alkalis:

(1) They are more sensitive to temperature differences. The activity of all is destroyed at a temperature below 100° and for each there is usually an optimum temperature.

(2) They are also sensitive to the acid or alkaline reaction of the substrate and for each enzyme very narrow limits of  $p_H$  give the best results.

(3) They are extremely readily poisoned, but can withstand antiseptics which kill most micro-organisms; strong antiseptics such as formaldehyde destroy their activity.

(4) It is not essential that the products obtained by the two processes should be identical. Thus in the case of the inversion of cane sugar by invertase the products are  $\alpha$ -glucose and  $\alpha$ -fructose, whereas when mineral acids are used the products are equilibrium mixtures of  $\alpha$ - and  $\beta$ -glucose and  $\alpha$ - and  $\beta$ -fructose, as the  $\alpha$ -glucose and the  $\alpha$ -fructose undergo immediate mutarotation in the presence of the mineral acid. Another example of a similar type is met with in the trisaccharide, raffinose; when hydrolysed by acid this yields galactose, fructose and glucose, the same sugar with raffinase yields melibiose and fructose, and with emulsin it yields galactose and sucrose. Similarly natural products of protein character yield comparatively simple amino-acids when hydrolysed with acids or alkalis, whereas with enzymes more complex intermediate products are formed.

(5) Although the processes of hydrolysis by acids and by enzymes are frequently compared it should be borne in mind that the rate at which a given substance is hydrolysed by the two different types of catalysts is frequently quite different, *e.g.* sucrose is hydrolysed by invertase much more readily than by a  $N$ -solution of hydrochloric acid; in fact, with a concentrated solution of invertase at 0° the inversion is practically instantaneous.

(6) An important point of difference between hydrolysis by means of acids or alkalis and hydrolysis under the influence of enzymes is that any particular enzyme has a very restricted use as a catalyst or the action of enzymes is essentially selective. Thus lipase can hydrolyse esters and not carbohydrates; maltase can hydrolyse maltose but not sucrose. That a slight difference in the configuration of two isomeric compounds is sufficient to affect their reactivities with a particular enzyme is shown in the case of the two stereoisomeric methyl-glucosides and of corresponding  $\alpha$ - and  $\beta$ -glycosides (both natural and synthetic). (*See* FERMENTATION AND GLYCOSIDES.)

The lipases, *e.g.* from castor oil or blood serum, hydrolyse glycerides in three distinct stages characterised by three velocity coefficients and corresponding with the elimination of the three acyl groups (Virtanen and Lindeberg, Suomen Kem. 1936, 9 B, 2), but do not readily hydrolyse ethyl esters (Reichel and Reimmuth, Z. physiol. Chem. 1936, 244, 78). Whereas pancreatic

lipase splits both ethyl esters and glycerides (Balls and Matlock, *J. Biol. Chem.* 1938, **123**, 678) but the former less rapidly. A careful study (Bamann and Rendelen, *Z. physiol. Chem.* 1936, **238**, 133; *cf. ibid.* 1933, **222**, 121; Langenbeck and Baltes, *Ber.* 1934, **67** [B], 1204) of the splitting of acid esters, dimethyl esters and methyl ester amides,



of the dibasic acids, malonic to adipic, by pigs' liver esterase and of the effects of altering  $\text{H}^+$  concentration and substrate concentration leads to the conclusion that the enzyme binding power of the ester group is controlled by the electrochemical nature of the adjoining groups. The carboxyl group inhibits the formation of the additive compound and can be counteracted or restricted by increasing the distance between the  $\text{CO}_2\text{Me}$  and  $\text{CO}_2\text{H}$  groups, by esterifying the  $\text{CO}_2\text{H}$  group or converting it into  $\text{CONH}_2$  and also by reducing the dissociation of the  $\text{CO}_2\text{H}$  group.

Pigs' esterase hydrolyses maleic esters (methyl to hexyl) more readily than the isomeric fumarates, oleic somewhat more readily than elaidic ester but erucic and brassidic esters at equal rates (Fabisch, *Biochem. Z.* 1931, **234**, 84).

Esterases, *e.g.* from human liver or pancreas, pigs' kidney or liver, are further characterised by producing asymmetric hydrolysis with a racemic ester, *e.g.* *dl*-ethyl mandelate or homologues, as one enantiomorph is hydrolysed more readily than the other (Ammon and Geisler, *Biochem. Z.* 1932, **249**, 470; *cf.* Dawson, Platt and Cohen, *Biochem. J.* 1926, **20**, 536). Similarly the *d*-form of the butyrate of phenylmethylcarbinol,  $\text{CHMePh} \cdot \text{OH}$ , is hydrolysed more readily than the *l*-form (*ibid.* 1932, **247**, 113; **249**, 446). By comparing the rates for *d*-, *l*- and *dl*-mandelates the ratio is 130:5:5 and with the *dl*-compound the *d* inhibits the hydrolysis of the *l* (Schwab and others, *Z. physiol. Chem.* 1933, **215**, 121). Many experiments have been made on the effect of adding compounds of different types; some accentuate the difference, others lessen it.

(7) Enzymes can act not merely as hydrolysing but also as synthesising agents. The process of hydrolysis is thus, in most cases, a balanced reaction, but the equilibrium is mainly in the direction of analysis and not synthesis. To obtain appreciable synthesis the amount of water must be restricted. The synthesising activity of an enzyme was first demonstrated by Croft Hill (*J.C.S.* 1898, **73**, 634; 1903, **83**, 578) in the case of maltase. The greater portion of the maltose is hydrolysed by the enzyme to glucose, but a certain proportion of disaccharide is always present.

A series of alkyl- $\beta$ -glucosides and galactosides has been synthesised by Bourquelot using emulsin, and  $\alpha$ -glucosides by an enzyme extracted from bottom yeast by means of water (*Ann. Chim.* 1913, [viii], **29**, 145; 1915, [ix], **3**, 287; 1915, [ix], **4**, 310; *cf. also* Bayliss, *J. Physiol.* 1913, **46**, 236).

Bayliss has synthesised arbutin from quinol and dextrose by means of emulsin in the presence of glycerol (*J.C.S.* 1912, **102**, i, 328). The synthetic action of enzymes in forming

polypeptides and proteins has also been demonstrated (Abderhalden, *ibid.* 1915, **108**, i, 725). Both glycogen and starch have been synthesised from glucose phosphoric acid (Hanes, *Nature*, 1940, **145**, 335).

Lipases and esterases also have synthesising properties; natural fats have been synthesised by the action of lipases on mixtures of glycerol and the higher fatty acids in the absence of a large excess of water. Esterases can give rise to asymmetric synthesis. The lipolytic enzymes present in certain seeds are made use of on a commercial scale for the preparation of fatty acids from natural fats (*cf.* Welter, *Z. angew. Chem.* 1911, **24**, 385; Pottevin, *Bull. Soc. chim.* 1906, [iii], **35**, 693). For details of the synthetic functions of enzymes, *see* FERMENTATION, ALCOHOLIC.

In some of these balanced actions between carbohydrates or esters and enzymes it has been shown that the equilibrium mixture is the same, whether mineral acid or enzyme is used, *e.g.* Visser's experiments using invertase and emulsin; in other cases, however, the equilibrium mixture with the enzyme is quite different from that obtained when an acid is used, *e.g.* Dietz's experiments with lipase and isoamyl *n*-butyrate (*Z. physiol. Chem.* 1907, **52**, 279).

The effects of numerous compounds on the hydrolytic activity of enzymes have been studied and a dilatometric method for studying ester formation and hydrolysis by esterase from pigs' pancreas developed (Ammon and Bartscht, *Biochem. Z.* 1934, **268**, 231).

*Glycosidic Enzymes.*—The rate of hydrolysis of phenyl- $\beta$ -*D*-glucoside by emulsin is not affected by cations, but anions increase the rate and the increase varies with the  $p_H$  value of the medium. The chlorate ion can increase it threefold. Increasing salt concentration increases the rate until a maximum is reached and the rate then remains constant (Helfferich, Schmitz-Hellebrecht, *Z. physiol. Chem.* 1935, **234**, 54). The enzymatic fission of glycosides is less in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$  if the enzyme is almost saturated with substrate, but if only a small amount of enzyme is combined with substrate the rate is more rapid in  $\text{D}_2\text{O}$  than in water (Salzer and Bonhoeffer, *Z. physikal. Chem.* 1936, **175**, 304).

*Amylases.*—Calcium chloride accelerates enzymatic amylolysis at certain values of  $p_H$ , and sodium chloride is less active (Baumgarten, *Biochem. J.* 1932, **26**, 539). Guanidine and creatine retard and creatinine accelerates such hydrolysis (Mystkowski, *ibid.*, p. 910). Carboxylic acids and amino-compounds retard and various proteins and amino-acids retard at values of  $p_H$  below but activate at values above  $p_H$  4.5 (Filipowicz, *ibid.* 1931, **25**, 1874). Dilute potassium cyanide or thionone can activate amylase (Borchardt and Pringsheim, *Biochem. Z.* 1933, **259**, 134).

*Esterases and Lipases.*—Glick and King (*J. Biol. Chem.* 1931, **94**, 497; 1932, **95**, 477; Weber and King, *ibid.* 1935, **108**, 131) find that *n*-alcohols have an inhibiting effect on esterase and that the effect increases as the series is ascended, but with the isomeric amyl alcohols there is a decrease in the effect as the steric hindrance around the OH increases; with secondary alcohols the effect of the steric factor

is eclipsed by that of the length of the carbon chain. The effect of the salts of fatty acids is small in the case of lipase but with esterase the effect increases up to *n*-laurate and then decreases almost to zero for palmitate and stearate. The effect of the salt of an unsaturated acid is greater than that of the saturated compound; hexyl and octyl alcohols have greater inhibiting powers than the corresponding sodium soaps and there appears to be a relationship between their activity and their effects in lowering surface tension. The butyl ether of glycol, unlike the ethyl ethers of both glycol and  $[-CH_2CH_2OH]_2$ , is fairly active against esterase but not lipase.  $CN$ ,  $I$ ,  $NO_3$ ,  $SH$ ,  $OH$ ,  $Cl$ ,  $CO$ ,  $CONH_2$ ,  $NH_2$ , attached to amyl or phenyl retard hydrolysis with esterase and benzylresorcinol has the greatest effect. The above series is similar to the lyotropic series of analogous ions in protein dispersion in aqueous solution. Glick and King (*ibid.* 1932, **97**, 675) find that the hydrolysis of tributyrin by pancreas lipase is accelerated in the decreasing order—hexylresorcinol, octyl alcohol, amyl iodide, hexyl alcohol, amyl alcohol, phenol, hexoic acid, cyclohexanol, resorcinol—and claim to demonstrate that the activation is due to concentration of the activator on the substrate resulting in a decrease of interfacial tension between enzyme and substrate. (*cf. also* Clark and Archibald (Trans. Roy. Soc. Canada, 1932, [n], **26**, III, 87).

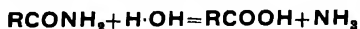
#### VI. THIOHYDROLYSIS, ALCOHOLYSIS, ACIDOLYSIS, AMMONOLYSIS.

Several types of reactions are analogous to hydrolysis and consist in the addition of a compound other than water, viz. hydrogen sulphide, alcohol or acid, to an ester or similar compound and the fission of the compounds to simpler compounds. Some of the commoner of such reactions are:

(1) **Thiohydrolysis.**—Esters of thioacetic acid are thiohydrolysed in liquid hydrogen sulphide into free acid and mercaptan just as carboxylic esters are hydrolysed by water to acid and alcohol. The degree of hydrolysis increases with the molecular weight of the ester, and even at  $-77^\circ$  is several times the value for the hydrolysis of the corresponding carboxylic ester at room temperature (Ralston and Wilkinson, J. Amer. Chem. Soc. 1928, **50**, 2160).

(2) **Alcoholysis.**—Reactions in which alcohols play much the same part as water in hydrolysis are usually grouped together under the name alcoholysis. The reaction with methyl alcohol is termed *methanolysis*, and that with ethyl *ethanolysis*.

The ethanolysis of an acid amide in the presence of a mineral acid is analogous to the hydrolysis of the amide by dilute mineral acids as shown by the two equations:



The latter reaction has been studied in detail by Reed (Amer. Chem. J. 1909, **41**, 483; J.C.S. 1913, **104**, 975). The reaction is bimolecular as the catalyst is gradually neutralised by the

ammonia formed in the reaction, and proceeds at an easily measurable rate at  $50^\circ$  in the case of benzamide. A determination of the ratio of *k* for *p*- and *m*-nitrobenzamide shows that this is 1.16, a value practically identical with the ratio for the hydrolysis of the two amides. The ratio of the constants for benzamide and *m*-nitrobenzamide varies considerably with the concentration of the hydrogen chloride. The effect of small amounts of water on the rate of alcoholysis is also marked, just as in the case of the esterification of an acid, and similarly *ortho*-substituents appear to have inhibiting effects. The general conclusion drawn is that the mechanism of alcoholysis is analogous to that of hydrolysis, and consists in the formation of salts between the amide and the mineral acid and the reaction of the complex cation with the alcohol. This alcoholysis occurs between thioamides and mercaptans (Reed, *l.c.*).

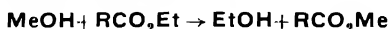
Another common type of alcoholysis met with is the conversion of an ester of a given acid into another ester of the same acid by means of an alcohol, *e.g.*:



This change does not take place readily except in the presence of a catalyst, the most efficient being sodium alkyl oxide (Purdie, J.C.S. 1885, **47**, 862; 1887, **51**, 627; 1888, **53**, 391; Clausen, Ber. 1887, **20**, 646), hydrogen chloride (Patterson and Dickinson, J.C.S. 1901, **79**, 280), sodium hydroxide (Henriques, Z. angew. Chem. 1898, **11**, 338; Pfannl, Monatsh. 1910, **31**, 301; Komnenos, *ibid.* 1910, **31**, 111, 687; 1911, **32**, 77; Kremann, *ibid.* 1905, **26**, 783; 1908, **29**, 23) or ammonia (Leuchs and Theodorescu, Ber. 1910, **43**, 1239). As a rule only a small amount of the catalyst need be used, but with the esters of aromatic acids saturation with hydrogen chloride is necessary. Bellet (Compt. rend. 1931, **193**, 1020; 1932, **194**, 1655) working with small amounts of sodium hydroxide proved that the rate of the reaction is reduced as the solution becomes neutral (due to hydrolysis of ester) but is increased with rise of temperature; that higher alcohols are readily displaced by lower and that tertiary are displaced more readily than primary. The reaction appears to be reversible, as it is possible to transform an ethyl into a methyl and conversely a methyl into an ethyl ester. The reaction is not limited to methyl and ethyl esters, but can be applied to more complex esters, such as benzyl and phenyl, and also to glyceryl esters (*cf.* Haller, *ibid.* 1906, **143**, 657; 1908, **146**, 259; Fanto and Stritar, Monatsh. 1908, **29**, 299), and is a most convenient laboratory method for the conversion of a given ester into another ester derived from the same acid. The esters of the great majority of aliphatic and aromatic acids react in this manner, but Sudborough and Edwards have shown that when the esters are derived from *diortho*-substituted benzoic acids the transformation cannot be effected by using either sodium alkyl oxide or saturating with hydrogen chloride and boiling for some time. Even when several substituents are present transformation occurs, provided the *ortho*-positions are free. This indicates that the transformation of esters under the influence of

hydrogen chloride is analogous to the esterification of an acid by the same catalyst.

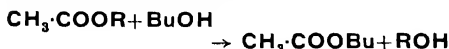
This analogy has been further confirmed by determining the rates of alcoholysis of various esters. These changes cannot be measured by a simple chemical method as in the case of esterification or hydrolysis, but use has been made of the volume changes which occur and the results obtained by dilatometric readings at constant temperature indicate that with an excess of the alcohol and using hydrogen chloride as catalyst the reaction



is practically unimolecular. The steric effects are very similar to those met with in the case of catalytic esterification (Kolhatkar, J.C.S. 1915, 107, 921). For further analogies between esterification and alcoholysis, cf. Sudborough and his co-workers (J. Indian Inst. Sci. 1914, 1, 107; 1918-20, 2, 121; 1920-21, 3, 1; 1921, 4, 181; 1922, 5, 1; 1924, 7, 1) and for alcoholysis of  $\beta$ -ketonic esters, see Connor and Adkins (J. Amer. Chem. Soc. 1932, 54, 3420), and for use of the Grignard reagent, e.g.

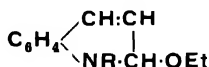


Ivanov and Roustchev (Compt. rend. 1932, 195, 467) who show that the heavy  $\text{R}''$  can replace the lighter  $\text{R}'$  in the ester and that if  $\text{R}'$  is aryl and  $\text{R}''$  aliphyl,  $\text{R}''$  partially replaces  $\text{R}'$  but that the reverse process proceeds to a very slight extent only. The reaction



is catalysed more actively by hydrogen chloride when  $\text{R}$ =bornyl, but more actively by potassium hydroxide when  $\text{R}$ =methyl.

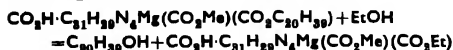
Similar transformations can be brought about in the case of the alkyl ethers of carbonium bases, e.g.



(Decker, J. pr. Chem. 1890, [iii], 45, 182), and of the oxygen ethers of substituted thiocarbamides, e.g.

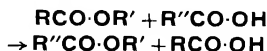


(Johnson and Guest, J. Amer. Chem. Soc. 1910, 32, 1279; cf. Kuntze, Arch. Pharm. 1908, 246, 110). An interesting case of alcoholysis observed by Willstätter and Stoll (Annalen, 1910, 378, 18) is the conversion of amorphous chlorophyll into crystalline chlorophyll by ethyl alcohol in the presence of an enzyme *chlorophyllase*, which accompanies chlorophyll in plant tissues. The reaction consists in the replacement of the complex phytol group by the simpler ethyl group



(3) *Acidolysis*.—Just as an ester reacting with an excess of an alcohol in the presence

of a catalyst can exchange its alkyl group, so the same ester in presence of excess of an acid and a catalyst can exchange its acyl group:



This was first studied by Reid (Amer. Chem. J. 1911, 45, 479) and subsequently in detail by Sudborough and Karve (J. Indian Inst. Sci. 1922, 5, 1) for the case of ethyl acetate and trichloroacetic acid where the values of  $k$  for the direct and reverse reactions are practically the same in the absence of a catalyst.

With ethyl acetoacetate and different acids the rate is not a simple function of the strength of the acid  $\text{R}''\text{CO}_2\text{H}$ . The reaction is catalysed by  $\text{H}_2\text{O}$  and conc.  $\text{H}_2\text{SO}_4$ , but not by gaseous  $\text{HCl}$  (Cherbuliez and Fuld, Arch. Sci. phys. nat. 1938, [v], 20, Suppl. 52).

A series of experiments by Sowa (J. Amer. Chem. Soc. 1938, 60, 654) using as catalyst  $\text{BF}_3 \cdot 2\text{AcOH}$  at  $100^\circ$  shows that  $n$ -propyl,  $n$ -butyl and *isopropyl* esters of propionic, benzoic and salicylic acids yield the corresponding acetates and that the yields are much smaller with *isopropyl*, *sec*-butyl and *tert*-butyl esters. A comparison of the catalysts  $\text{H}_2\text{SO}_4$ ,  $\text{ZnCl}_2$ ,  $\text{BF}_3$  and  $\text{BHF}_2(\text{OH})_2$  gives the percentage yields of  $n$ -butyl acetate as 20, 31, 40 and 60 respectively.

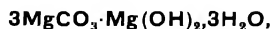
(4) *Ammonolysis*.—This term is sometimes applied to the reactions in which halogen atoms, sulphonic groups or alkoxy-groups are replaced by  $\text{NH}_2$  by using liquid ammonia or ammonia under pressure. With esters ammonium chloride acts as a catalyst and the effect of  $\text{R}$  in  $\text{CH}_3\text{R} \cdot \text{CO}_2\text{Et}$  is shown to be



(Audrieth and Kleinberg, J. Org. Chem. 1938, 3, 312). Many compounds are electrolytes in liquid ammonia (Groggins and Sturton, J. Ind. Eng. Chem. 1933, 25, 42, 169, 274).

J. J. S.

**HYDROMAGNESITE.** Hydrated basic carbonate of magnesium,



occurring as small, acicular or bladed (orthorhombic or monoclinic) crystals, but more often as white, earthy or chalky masses. It is a mineral of secondary origin, and usually occurs as veins in serpentine, from which it has been derived. It is softer and less heavy (sp.gr. 2.16) than magnesite. When calcined it can be used for the same purposes as magnesite. A large deposit is quarried at Atlin, in British Columbia (for analyses, see G. A. Young, Sum. Rep. Geol. Survey, Canada, 1915); and there is a considerable quantity available at a spot 93 miles north of Ashcroft, in the Lillooet district of British Columbia. Several occurrences are known in California. It is also found with the massive magnesite of Eubœa in Greece.

L. J. S.

"HYDRONALIUM" (v. Vol. I, 253b).

HYDRON YELLOW G (v. Vol. I, 423b).

**"HYDROPYRIN."** Trade name for lithium acetylsalicylate, which is claimed to be more soluble than aspirin and to combine the advantages of lithium salts and a specific for rheumatism.

**HYDROQUINENE** (v. Vol. III, 167c).

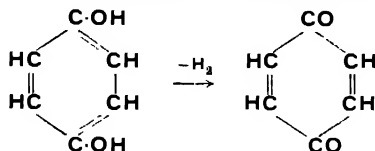
**HYDROQUINICINE** (v. Vol. III, 166c).

**HYDROQUINIDINE** (v. Vol. III, 164d).

**HYDROQUININE** (v. Vol. III, 166a).

**HYDROQUININONE** (v. Vol. III, 167a).

**HYDROQUINONE, QUINOL, 1:4-dihydroxybenzene.** The *p*-dihydroxy-derivatives of benzene and its homologues are readily oxidised to quinones and termed hydroquinones:



The oxidation is effected by nitric acid, chlorine, persulphate and other oxidising agents. A peculiarity of the reaction is the formation of a "half-way stage" in the oxidation. This highly coloured molecular compound of hydroquinone and quinone is called *quinhydrone*; it finds important applications in potentiometric and conductometric titrations. It has been suggested that it is a "zwitterion" between the benzenoid and quinonoid forms (Sidgwick, "Organic Chemistry of Nitrogen," 1937). Its autoxidation has been studied by R. Dubrisay and A. Saint-Maxen (Compt. rend. 1929, **189**, 694), A. Saint-Maxen (*ibid.* 1930, **191**, 212) and T. W. Evans and W. M. Dehn (J. Amer. Chem. Soc. 1930, **52**, 3204).

Hydroquinone occurs naturally, and by hydrolysis of natural products such as arbutin.

It is prepared synthetically by oxidation of phenol with alkaline permanganate (G.P. 81068) or with hydrogen peroxide (G. G. Henderson and R. Boyd, J.C.S. 1910, **97**, 1866), but in the laboratory it is usually prepared from aniline as follows: 25 g. of sodium dichromate dissolved in 100 ml. of water are added dropwise to 25 g. of aniline dissolved in 200 g. of concentrated sulphuric acid and 600 ml. of water, keeping the temperature below 100°C. The mixture at first becomes green, and towards the end of the reaction blue-black in colour. After standing overnight a further 50 g. of sodium dichromate in 200 ml. of water are added to the cooled solution. Most of the precipitate then dissolves, giving a turbid mixture containing quinone and quinhydrone in suspension. Sulphur dioxide is passed through, the suspended matter filtered off and the hydroquinone extracted from the filtrate with ether, which is subsequently distilled off. The product is purified by dissolving in the smallest quantity of hot water, a little sulphur dioxide passed through, boiled with charcoal, filtered and allowed to crystallise (L. Gattermann, "Die Praxis des organischen Chemikers," 12 Auf. 1914, pp. 249, 253).

Hydroquinone may also be prepared by heating *p*-chlorophenol to a high temperature, under pressure, with the addition of copper (G.P. 269544). An improved preparation of hydro-

quinone from quinhydrone is given in G.P. 380503; for the electrolytic reduction of quinone to hydroquinone, see Seyewetz and Miodon, Bull. Soc. chim. 1923, [iv], **33**, 449.

Hydroquinone is dimorphous, the stable form crystallising from water, the labile form being obtained by sublimation, m.p. 170-3°, b.p. 285°; sublimation commences about 10° below the melting-point. It is soluble in alcohol, ether and in hot water. Ferric chloride oxidises it to quinone and quinhydrone. In aqueous solution it gives no precipitate with lead acetate. Its alkaline solution darkens on exposure to air, and it reduces Fehling's solution in the cold and ammoniacal silver nitrate on warming. When heated with phthalic anhydride and zinc chloride it is converted into the colourless hydroquinonephthalein (F. Grimm, Ber. 1873, **6**, 506).

Hydroquinone condenses with amylene in the presence of sulphuric and acetic acids to give di-isoamylhydroquinone (W. Koenigs and C. Mai, *ibid.* 1892, **25**, 2650).

The very valuable property of hydroquinone of inhibiting oxidation, particularly of aldehydes, has been studied by C. Mourou and C. Dufrasse and others (Compt. rend. 1924, **179**, 1229; Bull. Soc. chim. 1924, [iv], **35**, 1564) (see Vol. V, 306a).

**HYDROQUINONE ETHERS.** The methyl and ethyl ethers of hydroquinone have recently found considerable use in perfumery. The ethyl ether is prepared by heating *p*-diazophenetole sulphate with dilute sulphuric acid, or by boiling hydroquinone with ethyl iodide and potassium hydroxide under a reflux condenser. It forms colourless needles melting at 66° and boiling at 247°. The dimethyl ether is a modern synthetic having a powerful odour resembling coumarin, and is employed in perfumes of the new-mown hay type. It forms colourless crystals melting at 55-56°.

E. J. P.

**HYDROQUINOTOXINE** (v. Vol. III, 166c).

**HYDROX POWDER** (v. Vol. IV, 562d).

**HYDROXYACETOPHENONES,** *o*-

*Hydroxyacetophenone*, HO·C<sub>6</sub>H<sub>4</sub>·CO·CH<sub>3</sub>. Prepared from phenol and acetic acid by heating with zinc chloride (H. Pauly and K. Lockemann, Ber. 1915, **48**, 30); together with *p*-hydroxyacetophenone by the rearrangement of phenyl acetate with aluminium chloride (K. Fries and W. Pfaffendorff, *ibid.* 1910, **43**, 215); and by heating diazotised *o*-aminoacetophenone prepared from *o*-nitrophenylpropionic acid (P. Friedlaender and J. Neudorfer, *ibid.* 1897, **30**, 1080). It is an oil, b.p. 106-107°/17 mm., 93-97°/10 mm. Acetyl derivative, m.p. 89°.

*m*-Hydroxyacetophenone.—Prepared from *m*-nitroacetophenone through the diazo-compound (Biginelli, Gazzetta, 1894, **24**, i, 440; E. Besthorn, E. Banzhaf and G. Jaeglé, Ber. 1894, **27**, 3042), m.p. 96°.

*p*-Hydroxyacetophenone, m.p. 108°.—Prepared from *p*-acetylanisole, by demethylation with hydrogen bromide (Charon and Zamanos, Compt. rend. 1901, **133**, 742).

*Resacetophenone*, 2:4-dihydroxyacetophenone.

—Prepared from resorcin and acetic acid by

heating with zinc chloride at 145–150° (Nencki and Sieber, J. pr. Chem. 1881, [ii], 23, 147), m.p. 142°C. Ferric chloride gives a wine-red colour with the aqueous solution.

**3:5-Dihydroxyacetophenone.**—Obtained by demethylation of the dimethyl ether with aluminium chloride in chlorobenzene solution (Mauthner, *ibid.* 1927, [ii], 115, 274).

**2:5-Dihydroxyacetophenone.**—May be prepared by heating 1 part hydroquinone with 1½ parts acetic acid and 1½ parts zinc chloride at 140–145° (Nencki and Schmid, *ibid.* 1881, [ii], 23, 546). Also by the rearrangement of hydroquinone diacetate (K. W. Rosenmund and H. Lohfert, Ber. 1928, 61 [B], 2605; R. W. Stoughton, R. Baltzy and A. Bass, J. Amer. Chem. Soc. 1934, 56, 2007). M.p. 202°. Crystallises from water in yellow-green crystals.

**Gallacetophenone** (2 : 3 : 4 - trihydroxyacetophenone).—Prepared by condensation of pyrogallol with acetic acid using zinc chloride (Nencki and Sieber, J. pr. Chem. 1881, [ii], 23, 151, 538). Also from acetyl chloride (6-23 parts) and pyrogallol (10 parts) by heating on a water bath (A. Einhorn and F. Hollandt, Annalen, 1898, 301, 107; E. Fischer, Ber. 1909, 42, 1015). M.p. 173°. Crystallises from water.

**HYDROXY-ACIDS.**—The hydroxy-acids are derived from the carboxylic acids by replacement of one or more hydrogen atoms in the hydrocarbon radical of the acid by one or more hydroxyl groups. The nomenclature is similar to that of the carboxylic acids (*q.v.*), for example, lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , may be called "α-hydroxypropionic acid" or "propan-2-ol-1-oic acid."

**Methods of Synthesis.**—The syntheses fall into three divisions; (I) introduction of the carboxyl group into the alcohol or phenol; (II) introduction of the hydroxyl group into the carboxylic acid; and (III) the simultaneous introduction of both hydroxyl and carboxyl group into the hydrocarbon molecule.

#### I. INTRODUCTION OF THE CARBOXYL GROUP INTO THE ALCOHOL OR PHENOL.

(i) Glycols, diprimary, primary secondary and primary tertiary, may be oxidised by dilute nitric acid or platinum black and air to the hydroxy-acid, *e.g.* propylene glycol to glycollic acid (A. Wurtz, Annalen, 1858, 105, 206; 107, 192).

(ii) By fusing the homologous phenols with alkalis when the alkyl group attached to the nucleus is oxidised to a carboxyl group. Salicylic acid is obtained by heating *o*-cresol with caustic soda with the addition of copper oxide at 260–270°, manganese at 250° or iron oxide at 300° (G.P. 170230; Chem. Zentr. 1906, II, 471).

(iii) Oxidation of phenolic aldehydes with alkali, *e.g.* salicylic acid from salicylaldehyde. The phenolic aldehydes may be prepared by the method of Tiemann and Reimer (*see* Gattermann, "Die Praxis des organischen (Chemikers," 12 Aufl., 1914, p. 318, Leipzig).

(iv) Carbon tetrachloride condenses with phenols to give a mixture of *o*- and *p*-carboxylic acids, the *p*-acid usually predominating, *e.g.* *p*-hydroxybenzoic acid from phenol, carbon

tetrachloride and caustic potash (K. Reimer and F. Tiemann, Ber. 1876, 9, 1285; G. Hasse, *ibid.* 1877, 10, 2186; G.P. 258887, using 40% caustic potash and copper powder).

(v) By hydrolysis of the hydroxy-cyanide, *e.g.* hydracrylic acid,  $\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , may be obtained by treating β-chloroethylalcohol with potassium cyanide and hydrolysing the nitrile with caustic soda solution (J. Wislicenus, Annalen, 1863, 128, 4; 1873, 167, 346; *see, however*, Erlenmeyer, *ibid.* 1878, 191, 278).

#### II. INTRODUCTION OF HYDROXYL GROUP INTO THE CARBOXYLIC ACID.

(i) Aldo-acids and keto-acids can be reduced with sodium amalgam or with zinc and hydrochloric or sulphuric acid, *e.g.* lactic acid from pyruvic acid. Glycollic acid may be obtained by the reduction of oxalic acid with zinc (A. H. Church, J.C.S. 1863, 16, 302).

(ii) The most important method is by the replacement of halogen by hydroxyl in halogeno-carboxylic acids by means of a metal oxide or hydroxide, *e.g.* silver oxide or alkali hydroxide. Water is often sufficient to replace a labile halogen atom without the use of metal hydroxide, *e.g.* glycollic acid from monochloroacetic acid (G. C. Thomson, Annalen, 1880, 200, 76); hydracrylic acid from β-bromopropionic acid (W. Lossen and E. Kowski, *ibid.* 1905, 342, 128); γ-butyrolactone from γ-chlorobutyric acid (Henry, Bull. Soc. chim. 1886, [ii], 45, 341).

(iii) Treatment of the amino-acids with nitrous acid ( $\text{NaNO}_2 + \text{HCl}$ ), followed by warming in the case of aromatic amines, replaces the  $\text{NH}_2$  group by  $\text{OH}$ , *e.g.* glycollic acid from glycine, and salicylic acid from anthranilic acid.

(iv) By treating unsaturated acids with hydrobromic acid or with dilute sulphuric acid, *e.g.* γ-valerolactone from allylacetic acid.

#### III. SIMULTANEOUS INTRODUCTION OF BOTH HYDROXYL AND CARBOXYL GROUPS.

(i) Hydrogen cyanide followed by hydrochloric acid on aldehydes and ketones as well as on ethylene oxides gives finally an acid with the hydroxyl group in the α-position to the carboxyl group in the case of aldehydes and ketones.



The cyanohydrin first formed is hydrolysed to the acid by hydrochloric acid. In the preparation of mandelic acid, benzaldehyde bisulphite compound is treated with sodium cyanide and the mandelonitrile hydrolysed with concentrated sulphuric acid ("Organic Syntheses," Coll. Vol. I, New York, 1932, p. 329). Other preparations are those of lactic acid from acetaldehyde (Simpson and Gautier, Compt. rend. 1867, 65, 418), and hydracrylic acid from ethylene oxide (Erlenmeyer, Annalen, 1878, 191, 278).

(ii) By fusion of the arylsulphonic acid with alkalis, *e.g.* salicylic acid from *o*-toluenesulphonic acid (Wolkow, Z. Chem. 1870, 326).

(iii) By passing air at 160° through paraffin



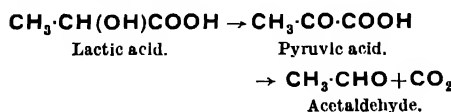
wax (m.p. 52°), mixtures of hydroxy-acids are produced, e.g.



(P. P. Schorigin and A. P. Kreshkov, Amer. Chem. Abstr. 1934, 28, 6106; 1935, 29, 2147).

**Properties.**—The hydroxy-acids are divided into two classes, the alcoholic acids and the phenolic acids, having some properties in common, such as the replacement of the hydrogen of the hydroxyl group by metals or alkyl groups. In the case of alcohols, alkali metal is necessary, but caustic alkali will replace the more acidic hydrogen of the phenol. Acid chlorides replace the hydroxyl hydrogen of the phenol or alcohol giving the corresponding ester. The carboxyl group yields the normal ester, amide, nitrile and salts.

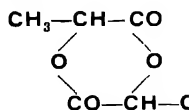
In the aliphatic series hydriodic acid reduces the hydroxy-acids to the corresponding fatty acid, e.g. propionic acid from lactic acid. The aliphatic hydroxy-acids are in general more soluble in water but less so in ether than the corresponding fatty acids and are less volatile and cannot as a rule be distilled. On oxidation or by the application of heat the aliphatic hydroxy-acids show different properties according as they are  $\alpha$ -,  $\beta$ - or  $\gamma$ -hydroxy-acids, e.g. hydraacrylic acid, a primary hydroxy-acid,  $HO\cdot CH_2\cdot CH_2\cdot COOH$ , yields semi-malonic aldehyde and malonic acid as primary products. Secondary hydroxy-acids, e.g. lactic acid,  $CH_3\cdot CH(OH)COOH$ , yield ketonic acids. The  $\alpha$ -ketonic acids change to aldehyde and carbon dioxide, e.g.



Tertiary  $\alpha$ -hydroxy-acids yield ketones, e.g.  $\alpha$ -hydroxyisobutyric acid,

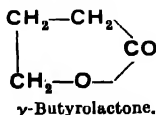


$\alpha$ -Hydroxy-acids on heating lose water and become cyclic double esters—the lactides, e.g. lactic acid gives

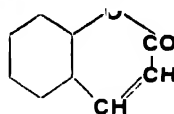


$\beta$ -Hydroxy-acids lose water and become unsaturated acids, thus hydraacrylic acid becomes acrylic acid.

$\gamma$ - and  $\delta$ -Hydroxy-acids lose water at the ordinary temperature and change more or less completely into simple cyclic esters—the lactones.



This property is shared by some phenolic acids such as coumaric acid which gives



Coumarin.

The phenolic acids decompose into the phenol and carbon dioxide when distilled with soda-lime. The  $o$ -acids give a deep violet colour with ferric chloride, and are volatile in steam, in contrast to the  $m$ - and  $p$ -acids which are not volatile and give no distinctive colour with ferric chloride. The  $m$ -acids are the most stable and are converted into hydroxyanthraquinones when heated with concentrated sulphuric acid. Boiling hydrochloric acid decomposes the  $p$ -acids into  $CO_2$  and phenols. S. Krishna and F. G. Pope (J.C.S. 1922, 121, 798) find that the action of potassium iodide and iodate on some aromatic hydroxy-acids is to give the tri-iodophenol, the carboxyl group being eliminated. Thus salicylic acid and  $p$ -hydroxybenzoic acid both give 2:4:6-tri-iodophenol; 3- or 5-nitrosalicylic acid gives tri-iodonitrophenol and 3:5-dinitrosalicylic acid gives tri-iododinitrophenol. (See CARBOXYLIC ACIDS,  $\beta$ -HYDROXYBUTYRIC ACID and HYDROXYSTEARIC ACIDS.)

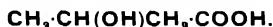
$\alpha$ - and  $\beta$ -HYDROXYANTHRAGALLOL (v. Vol. I, 212d).

HYDROXYANTHRAPURPURIN (v. Vol. I, 213a).

$\beta$ -HYDROXYANTHRAQUINONE (v. Vol. I, 212d).

HYDROXYANTHRARUFIN (v. Vol. I, 224c).

$\beta$ -HYDROXYBUTYRIC ACID,



Prepared by the reduction of acetoacetic ester with sodium amalgam (J. Wislicenus, Annalen, 1869, 149, 205); or by the action of potassium cyanide on  $\alpha$ -propylenechlorohydrin and hydrolysis of the resulting nitrile (W. Markownikoff, *ibid.* 1870, 153, 237). It is a thick syrup volatile in steam and decomposes on heating into water and crotonic acid. It has been resolved into its optical enantiomorphs by means of the quinine salts (A. McKenzie, J.C.S. 1902, 81, 1402).  $l$ - $\beta$ -Hydroxybutyric acid occurs in the urine in considerable quantities in cases of *diabetes mellitus* and is the source of acetone in the urine. For its detection in urine, see Molhan (Bull. Soc. chim. Belg. 1924, 33, 261); Bierry and Moquet (Compt. rend. 1924, 178, 816); Engfeldt (Biochem. Z. 1924, 144, 556; cf. Lublin, *ibid.* 1924, 147, 187, and Goldblatt, Biochem. J. 1925, 19, 626).

HYDROXYCHRYSAZIN (v. Vol. I, 212d).

**HYDROXYCITRONELLAL.** This valuable synthetic perfume is a somewhat variable commercial product, in which citronellal hydrate predominates. It is very liable to polymerisation and should be stored in full containers in the

dark. The main constituent has the following constitution :



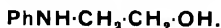
The best commercial samples have  $d^{25}_D$  about 0.930; optical rotation  $+8^\circ$  to  $+10^\circ$ ;  $n^{20}_D$  1.448-1.455.

It is a viscous liquid with a fine lily of the valley note, and is valuable in muguet, hyacinth, narcissus, sweet pea and lily of the valley perfumes.

E. J. P.

**HYDROXYEREMOPHILONE** (v. Vol. IV, 324c)

$\alpha$ -HYDROXYETHYLANILINE,



Prepared by heating equimolecular quantities of aniline and ethylene chlorohydrin under pressure at  $110^\circ$  (Knorr, Ber. 1889, 22, 2092), or by boiling under a reflux aniline (2 mols.) and ethylene chlorohydrin (1 mol.) with water (G.P. 163043). It has b.p.  $286^\circ$ ,  $167^\circ/17$  mm.;  $d^{20}_D$  1.11, is slightly soluble in water, readily so in alcohol and ether; it yields indoxyl on fusion with alkali.

**HYDROXYFLAVOPURPURIN** (v. Vol. I, 212d).

$\beta$ -HYDROXYGLUTAMIC ACID (v. Vol. I, 318c).

**HYDROXYLAMINE**,  $\text{NH}_2\text{OH}$ . Discovered by W. Lossen (Annalen, Suppl. 1808, 6, 220) in 1865, but only known in the form of its salts or in aqueous solution until 1891.

It may conveniently be prepared in the laboratory by the following method: 2 mol. of commercial sodium nitrite in concentrated aqueous solution and 1 mol. of sodium carbonate are kept at  $-2^\circ$  to  $-3^\circ$  with constant stirring, and sulphur dioxide passed in until just acid. The solution is warmed gently with a few drops of sulphuric acid and kept at  $90-95^\circ$  for 2 days. It is then neutralised with sodium carbonate, concentrated by evaporation to  $10\frac{1}{2}$ -11 times the weight of nitrite taken and sodium sulphite allowed to crystallise out by cooling. Hydroxylamine sulphate left in the mother liquor may be purified by crystallisation (E. Divers and T. Haga, J.C.S. 1887, 52, 661; 1896, 70, 1665). For a modification of this process giving a 70% yield of the pure hydrochloride, see Organic Syntheses, 1923, III, 65.

Much work has been done on the electrolysis of nitric acid, nitrous acid and other derivatives to produce hydroxylamine salts (G.P. 133457, 137697; J.S.C.I. 1902, 21, 1458; F.P. 322943; J.S.C.I. 1903, 22, 425; J. Tafel, Z. anorg. Chem. 1902, 31, 289; E. P. Schoch and R. H. Pritchett, J. Amer. Chem. Soc. 1916, 38, 2042). J. Stöcherbakow and D. Libina (Z. Elektrochem. 1929, 35, 70, 826) and G. Ponzio and A. Pichetto (Annali Chim. Appl. 1924, 14, 250) have studied the electrolytic reduction of nitric acid to hydroxylamine.

It may also be prepared by the reduction of nitric acid with metals under suitable conditions (E. Divers, J.C.S. 1883, 43, 443; 1885, 47, 597). Nitrates, nitrites, nitro-bodies, etc., in neutral solution are reduced by finely divided

metals to give hydroxylamine (B. P. 11216/1894; J.S.C.I. 1895, 14, 595).

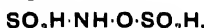
Catalytic methods include the reduction of nitric acid by hydrogen in the presence of spongy platinum at  $115-120^\circ$  (A. Jouve, Compt. rend. 1899, 128, 435).

To isolate free hydroxylamine, the hydrochloride is dissolved in methyl alcohol and sodium methoxide in methyl alcohol added. The sodium chloride is filtered off and the alcohol removed by distillation under reduced pressure. Hydroxylamine distils at about  $70^\circ/60$  mm., and about  $58^\circ/32$  mm. Vaseline may be added to inhibit frothing during distillation, and care should be taken to exclude air as at  $60-70^\circ$  explosive mixtures may be formed (C. A. Lobry de Bruyn, Rec. trav. chim. 1891, 10, 100; 1893, 11, 18; J. W. Brühl, Ber. 1894, 27, 1347). L. Crismer obtained the anhydrous substance by passing ammonia through the complex salt, dihydroxylamine zinc chloride,  $\text{ZnCl}_2 \cdot 2\text{NH}_2\text{OH}$ , distilling off first the solvent ether and then the hydroxylamine (Bull. Soc. chim. 1891, [iii], 6, 793). R. Uhlenhuth (Annalen, 1900, 311, 117) obtained it by distillation of the phosphate under reduced pressure. O. Baudisch and F. Jenner (Ber. 1916, 49, 1182) added the dry, finely powdered sulphate to liquid ammonia in a quartz tube, removed the ammonia and extracted the hydroxylamine with alcohol. Owing to the danger from explosion attending the distillation of hydroxylamine, H. Lecher and J. Hofmann (*ibid.* 1922, 55 [B], 912) prepared the free base by suspending the hydrochloride in absolute alcohol, adding a solution of sodium ethoxide in absolute alcohol, filtering off the sodium chloride and cooling the filtrate to  $-18^\circ$  when  $\text{NH}_2\text{OH}$  crystallised out.

Hydroxylamine forms white inodorous scales or hard needles, sp.gr. about 1.3, m.p.  $33^\circ$ , b.p.  $56-57^\circ/22$  mm. When kept at ordinary pressures above  $15^\circ$  hydroxylamine darkens; at higher temperatures explosion is likely to occur. Readily soluble in water and to a less extent in ethyl and methyl alcohols, and in boiling ether. It is decomposed by alkali giving nitrogen, nitrous oxide, nitrous acid and water (S. S. Kolotoff, J. Russ. Phys. Chem. Soc. 1891, 23, 3). The aqueous solution is colourless and odourless and has a strongly alkaline reaction. In many of its properties hydroxylamine resembles ammonia but it is less basic. For example, Zn, Fe, Ni, Al, Cu, are precipitated from their soluble salts as hydroxides insoluble in excess, but the alkaline earths are not precipitated. It acts as a strong reducing agent, e.g. with  $\text{CuSO}_4$  solution red  $\text{Cu}_2\text{O}$  is precipitated,  $\text{HgCl}_2$  is reduced to  $\text{Hg}_2\text{Cl}_2$  and Ag, Au, and Pt are precipitated from their salts. In alkaline solution it converts ferrous to ferric hydroxide, whilst in acid solution it reduces ferric to ferrous salts.

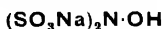
The salts of hydroxylamine are readily soluble in water and alcohol, crystallise well and are anhydrous. The three hydrogen atoms of hydroxylamine are replaceable by sulphonic acid groups, e.g.  $\beta\beta$ -hydroxylaminedisulphonic acid ( $\text{SO}_3\text{H}_2\text{N}:\text{OH}$  (Raschig, Chem.-Ztg. 1888, 12, 219), the alkali salts of which are stable.

For the  $\alpha\beta$ -trisulphonic acid derivative,  $(\text{SO}_3\text{H})_2\text{N}\cdot\text{O}\cdot\text{SO}_3\text{H}$ , and the  $\alpha\beta$ -disulphonic acid (or isodisulphonic acid)



see F. Raschig, Ber. 1923, 56 [B], 206.

Hydroxylamine hydrochloride or



reacts with furfuraldehyde at 155–160° under pressure to give 2:5-dihydroxypyridine (K. Aso, A. 1930, II, 386). Complex salts analogous to the amines have been prepared (Goreminkin and Gladishevskaja, A. 1939, I, 533).

Hydroxylamine and its salts have been used as photographic developers and for recovering silver from fixing baths (Lamer, J.S.C.I. 1890, 9, 890); as a substitute for chrysarobin and pyrogallol (Schwarz, Pharm. Ztg. 33, 659). Manganese brown has been discharged by application of the hydrochloride (Schaeffer, Bull. Mulhouse, 1883; see also J.S.C.I. 1884, 3, 166).

Hydroxylamine has been reported in the cells of *Chlorella*, formed under ordinary conditions of growth (D. Michlin, A. 1938, III, 1062). Its formation in culture media from the reduction of nitrates by micro-organisms has been reported (J. Blom, Biochem. Z. 1928, 194, 385). See also papers by M. Lemoigne, P. Monguillon and R. Desveaux (Bull. Soc. Chim. Biol. 1938, 20, 441) on hydroxylamine in biological processes.

It is used for preparing oximes of aldehydes and ketones. Aldoximes are usually prepared by adding the aldehyde (1 mol.) to an aqueous solution of hydroxylamine hydrochloride (1 mol.) and sodium carbonate (1½ mol.). Aqueous alcohol is used for water-insoluble aldehydes. Ketoximes are somewhat more difficult and are prepared by heating the calculated quantity of ketone, hydroxylamine hydrochloride and sodium acetate in aqueous or alcoholic solution 1–2 hours on a water bath. Also by heating the ketone dissolved with alcohol, and  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , in a sealed tube for 8–10 hours at 160–180° (I. Schmidt Houben, "Die Methoden der organischen Chemie," 3 Aufl. 1930, 584). Certain oximizations may be carried out by the use of sodium hydroxylamine monosulphonate,

For a laboratory preparation of this reagent, see Organic Syntheses, 1930, X, 23. For the determination of the aldehyde in oil of citronella with hydroxylamine hydrochloride, see Vol. III, 191c. For the use of hydroxylamine in the determination of camphor, see Vandoni and Deseigne, Bull. Soc. chim. 1935, [v], 2, 1685.

**Detection and Estimation.**—Hydroxylamine may be detected by its reducing properties on silver nitrate, and Fehling's solution. By adding sodium nitroprusside to a neutral solution and a little caustic soda, a magenta-red coloration is produced (A. Angeli, Gazzetta, 1893, 23, ii, 102). It yields benzhydroxamic acid on treatment with sodium acetate and benzoyl chloride and this gives a violet-red coloration with ferric chloride (E. Bamberger, Ber. 1899, 32, 1805). As little as 0.0001 g. can be detected colorimetrically by means of *p*-bromonitrosobenzene and  $\alpha$ -naphthol (J. Blom,

Biochem. Z. 1928, 194, 385). Another sensitive test depends on the formation of a fugitive purple coloration on treatment with yellow ammonium sulphide and excess of ammonia (W. M. Fischer, Chem.-Ztg. 1923, 47, 401). An ammoniacal solution of diacetylmonoxime with hydroxylamine forms dimethylglyoxime which can be identified by its reaction with nickel salts. Hydroxylamine gives with resorcinol and potassium periodate in solution buffered to  $p_H$  2, a stable cherry-red colour—reported sensitivity 1 part per million (G. G. Rao and W. V. B. S. Rao, Analyst, 1938, 63, 718).

It may be estimated by titration in alkaline solution with mercury acetamide, which is reduced to metallic mercury (M. O. Forster, J.C.S. 1898, 74, 785); by oxidation with vanadic sulphate, measuring the nitrogen evolved and titrating the vanadous sulphate with potassium permanganate (K. A. Hofmann and F. Kuspert, Ber. 1898, 31, 64); also by adding excess of standard titanium trichloride and back-titrating the excess with potassium permanganate (A. Stahler, *ibid.* 1904, 37, 4732; *ibid.* 1909, 42, 2695). Of three methods investigated by W. C. Bray, M. E. Simpson and A. A. MacKenzie (J. Amer. Chem. Soc. 1919, 41, 1363) the two following methods were found to be accurate: (1) Reduction to ammonia by excess of titanous salt in acid solution, and (2) oxidation to nitrous oxide by excess ferric sulphate in sulphuric acid solution with subsequent titration of the ferrous salt with permanganate. Also it may be estimated by adding an excess of  $0\cdot1\text{N}\text{KBrO}_3$  solution and sulphuric acid, and after ½–1 hour adding potassium iodide solution and titrating the liberated iodine with sodium thiosulphate (A. Kurtenacker and J. Wagner, Z. anorg. Chem. 1922, 120, 261).

For the colorimetric determination, see W. Pucher and H. A. Day (J. Amer. Chem. Soc. 1926, 48, 672). The method depends on Bamberger's benzhydroxamic acid reaction with ferric chloride (*v. supra*). For the determination of small quantities of the order of 1 mg. in 4 c.c., the hydroxylamine is oxidised by iodine to nitrous acid which is determined photometrically by the diazo-method, using sulphanilic acid and  $\beta$ -aminonaphthalene in acetic acid. Error  $\pm 2\cdot3\%$  for  $0\cdot1\text{--}0\cdot2 \times 10^{-6}$  g. in 10 c.c. The method can be extended to solutions containing nitrite and nitrate (G. Endres and L. Kaufmann, Annalen, 1937, 530, 184). Hydroxylamine has also been determined coulometrically (L. Szebellédy and Z. Somogyi, Z. anal. Chem. 1938, 112, 400).

**Ethylhydroxylamines v. ETHYL.**

**$\beta$ -Phenylhydroxylamine,  $\text{NHPh}\cdot\text{OH}$ .**—

This compound may be prepared by the reduction of nitrobenzene with zinc dust in ammonium chloride solution (C. S. Marvel and O. Kamm, J. Amer. Chem. Soc. 1919, 41, 279; Organic Syntheses, 1932, Coll. Vol. I, 435, yield 62–68%). Consistently good yields are obtained if the zinc dust is previously treated with 2% mercurous nitrate solution slightly acidified with nitric acid (Kasanof, Ind. Eng. Chem. 1920, 12, 799). Many other methods have been recorded for its preparation: oxidation of aniline with Caro's acid in the presence of ether

at 0° (E. Bamberger and F. Tschirner, Ber. 1899, **32**, 1675) or electrolytically in acetic acid solution (Haber, Z. Elektrochem. 1898, **5**, 77); by the reduction of nitrobenzene with zinc amalgam in an aqueous-alcoholic solution of aluminium sulphate (E. Bamberger and M. Knecht, Ber. 1896, **29**, 863); or with zinc dust in the presence of calcium chloride in ether or alcohol solution (C. Goldschmidt, *ibid.* 2307; G.P. 84138; see also Wislicenus, J. pr. Chem. 1896, [ii], **54**, 57). The substance is very poisonous and should not be allowed to come in contact with the skin (O. Baudisch, Chem.-Ztg. 1911, **35**, 913).

$\beta$ -Phenylhydroxylamine forms colourless needles, m.p. 81–82°; soluble in 10 parts hot and 50 parts cold water, readily soluble in alcohol, ether, carbon disulphide and chloroform, sparingly soluble in light petroleum. Ammoniacal silver nitrate and Fehling's solution are reduced in the cold by  $\beta$ -phenylhydroxylamine. Mineral acids yield *p*-aminophenol and azoxybenzene; alcoholic sulphuric acid gives azoxybenzene, *o*- and *p*-phenetidine, *o*- and *p*-aminophenol, aniline and other compounds (E. Bamberger and J. Lagutt, *ibid.* 1898, **31**, 1501). It dissolves in sulphuric acid with a deep blue colour. By heating at 100°, azobenzene together with aniline, azoxybenzene and other products are formed. Oxidation with permanganate gives first nitrosobenzene then nitrogen and azoxybenzene (E. Bamberger and F. Tschirner, Ber. 1899, **32**, 342). It dissolves in sodium hydroxide giving a sodium salt, which decomposes into nitrobenzene and azoxybenzene in the presence of air but into azoxybenzene and aniline if air is excluded (E. Bamberger and F. Brady, *ibid.* 1900, **33**, 271). With aromatic aldehydes it yields phenylaldoximes of the type



(G. Plancher and G. Piccinini, Atti. R. Accad. Lincei, 1905, [v], **14**, ii, 36). The 2:4-dinitro-derivative,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{NH}\cdot\text{OH}$ , is made by the action of an alcoholic solution of hydroxylamine on 2:4-dinitrodiphenyl ether. It has marked acidic properties and gives intensely coloured ammonium and aniline salts (W. Borsche, Ber. 1923, **56** [B], 1944).

#### Nitroso- $\beta$ -phenylhydroxylamine,



may be conveniently prepared by the action of sodium nitrite and dilute sulphuric acid on  $\beta$ -phenylhydroxylamine (A. Wohl, *ibid.* 1894, **27**, 1435; E. Bamberger, *ibid.* 1953) or by the interaction of hydroxylamine and nitrobenzene in alcoholic solution in the presence of sodium ethoxide (A. Angeli, *ibid.* 1896, **29**, 1884). It crystallises from light petroleum, m.p. 58–59°, and decomposes at 75°. Readily soluble in organic solvents, sparingly so in water. Alcoholic or ethereal solutions give a brownish-red coloration with a few drops of ferric chloride.

The most important derivative is the ammonium salt, *cupferron*,  $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$ , and is prepared as follows: An ice-cold solution of 25 g. nitrobenzene in 125 c.c., 96% alcohol and

25 c.c. water is saturated with ammonia and then treated with hydrogen sulphide for 24–3 hours. To the resulting pale yellow, pasty mass, 500 c.c. ether are added, the solution shaken vigorously and filtered. The ether layer is separated and saturated with ammonia, withdrawn, cooled in ice and ethyl nitrite vapour passed in ( $\text{NaNO}_2$  25 g.,  $\text{H}_2\text{O}$  40 c.c., 96%  $\text{C}_2\text{H}_5\cdot\text{OH}$  33 c.c. and 1:1  $\text{HCl}$  90 c.c.). The solution becomes dark at first, the colour slowly disappears and crystals of cupferron separate. It is washed with ether and dried over calcium chloride and ammonium carbonate. Yield 80% (K. H. Slotta and K. R. Jacobi, Z. anal. Chem. 1930, **80**, 97). See also Organic Syntheses, 1932, Coll. Vol. I, 171.

The microcrystalline forms of several salts of nitroso- $\beta$ -phenylhydroxylamine have been found to be sufficiently characteristic to be employed in the identification of the particular metal (Martini, Mikrochem. 1928, **6**, 152). Cupferron has been used to separate zirconium and uranium (Angeletti, Gazzetta, 1921, **51**, 285).

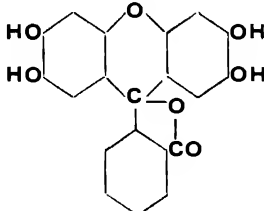
Cupferron is a brownish-white crystalline soluble substance and yields well-defined coordination compounds when its ammonium radical is replaced by many of the metals. It is most useful in the separation of iron, titanium and zirconium, since it precipitates these elements from strongly acid solutions containing aluminium, chromium, manganese, nickel, cobalt, zinc, magnesium and the alkaline earths. The ferric and copper salts may be separated by dissolving out the latter with ammonium hydroxide. The ferric salt is soluble in chloroform, ether, acetone, etc., and may be dissolved and separated from other salts, such as those of lead, silver or tin, which may have been precipitated with it (Baudisch, Chem.-Ztg. 1909, **33**, 1298; 1911, **35**, 913; H. Biltz and O. Hottke, Z. anorg. Chem. 1910, **66**, 426; J. Hanuš and A. Soukup, *ibid.* 1910, **68**, 52; R. Fresenius, Z. anal. Chem. 1911, **50**, 35). See also CHEMICAL ANALYSIS and Lundell and Knowles, Ind. Eng. Chem. 1920, **12**, 344, for further applications.

#### HYDROXYPROLINE (v. Vol. I, 317c).

**HYDROXYQUINOL**, 1:2:4-trihydroxybenzene. This substance is obtained by rapidly heating hydroquinone with 8–10 times its weight of caustic soda until evolution of hydrogen has almost ceased (Barth and Schreder, Monatsh. 1883, **4**, 176); or by dissolving 150 g. quinone in 400–450 g. acetic anhydride and 10 c.c. concentrated sulphuric acid, keeping the temperature at 40–50°, and finally pouring into much water. The precipitated hydroxyhydroquinone triacetate is saponified with a methyl alcoholic solution of sulphuric acid, neutralised with anhydrous sodium carbonate, extracted with ether, filtered and the solvent removed. The residue is allowed to crystallise in a vacuum desiccator (Thiele, Ber. 1898, **31**, 1248).

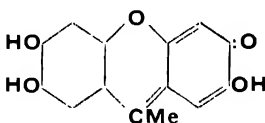
It crystallises from ether in microscopic scales, m.p. 140–5°, and distils with partial decomposition to give quinol. Its aqueous solution darkens rapidly on exposure to the air, and ferric chloride solution gives a transient bluish-green coloration, which changes to dark blue, and then to wine-red on the careful addition of sodium carbonate solution.

Hydroxyquinol (2 mol.) when heated with phthalic anhydride (1 mol.) to 185–190° gives hydroxyquinolphthalein,



(W. Feuerstein and M. Dutoit, *ibid.* 1901, **34**, 2637).

Condensation takes place with aldehydes. Using concentrated sulphuric acid in alcoholic solution, paraldehyde gives the compound:



(C. Liebermann and S. Lindenbaum, *ibid.* 1904, **37**, 1177, 2731).

For an account of the derivatives, see Bargellini (Gazzetta, 1910, **40**, ii, 342; 1911, **41**, ii, 612; 1912, **42**, ii, 351; Atti. R. Accad. Lincei, 1911, [v], **20**, i, 22; ii, 18, 118, 183). The trimethyl ether has been used by J. Reigrodski and J. Tambor (Ber. 1910, **43**, 1964) for the synthesis of 2:3-dihydroxyflavone.

**HYDROXYSTEARIC ACIDS**, *α*-Hydroxystearic Acid,



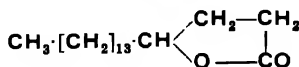
Prepared by treating *α*-bromostearic acid with aqueous potash. Separates from a mixture of benzene and light petroleum as a crystalline powder, m.p. 91–92° (C. Hell and J. Sadowsky, Ber. 1891, **24**, 2391; H. R. Le Sueur, J.C.S. 1904, **85**, 827). By heating to 270° it yields margaric aldehyde,  $\text{C}_{16}\text{H}_{33}\text{CHO}$ , a lactide,  $\text{C}_{32}\text{H}_{68}\text{O}_4$ , formic acid and carbon dioxide. (Le Sueur, *l.c.*)

*β*-Hydroxystearic Acid,



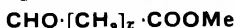
Prepared by treating *β*-bromostearic acid with aqueous potash. Crystallises from chloroform in white plates, m.p. 89° (Ponzio, Gazzetta, 1905, **85**, ii, 570).

*γ*-Hydroxystearic Acid.—Exists most commonly in the form of its lactone,



which is prepared by heating oleic acid with concentrated sulphuric acid at 80–85° for 6 hours, diluting with water and warming on a water bath; it has m.p. 52–53°, and yields the acid, m.p. 89°, on heating with alkali and finally acidifying with hydrochloric acid (P. W. Clutterbuck, J.C.S. 1924, **125**, 2330).

C. G. Tomecko and R. Adams (J. Amer. Chem. Soc. 1927, **49**, 522) by condensing aldehyde esters of the general formula,



(where  $x=7, 8, 9, 10, 11$ ) with the Grignard reagent,  $\text{CH}_3 \cdot [\text{CH}_2]_y \cdot \text{MgBr}$  (where  $y=8, 7, 6, 5, 4$ ) have obtained the esters of the following hydroxystearic acids, from which the pure acids are obtained by hydrolysis,



	M.p., ester.	M.p., methyl ester.
8 or <i>θ</i> -hydroxystearic acid .	74–75°	45–46°
9 or <i>ι</i> -hydroxystearic acid .	81–82°	53–54°
10 or <i>κ</i> -hydroxystearic acid .	76–77°	49–50°
11 or <i>λ</i> -hydroxystearic acid .	78–79°	50–51°
12 or <i>μ</i> -hydroxystearic acid .	77–77.5°	52–52.5°

*ι*-Hydroxystearic acid may also be prepared by the action of sulphuric acid on oleic acid (Tscherbakow and Saizew, J. pr. Chem. 1898, [ii], **57**, 27). At 100° it yields the anhydride, and oxidation with chromic acid in acetic acid converts it into sebacic, azelaic and traces of suberic and a liquid monobasic acid, together with *ι*-ketostearic acid,



m.p. 76°. On distillation, *ι*-hydroxystearic acid gives  $\Delta^4$ -claidic and  $\Delta^6$ -claidic acids and ordinary oleic acid (Vesely and Majtl, Chem. Listy, 1925, **19**, 345; Bull. Soc. chim. 1926, [iv], **39**, 230).

*κ*-Hydroxystearic Acid,



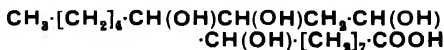
Prepared by the action of sulphuric acid on isooleic acid, Shukow and Schestakow (J. Russ. Phys. Chem. Soc. 1903, **35**, 1) who give the m.p. as 84–85°. Oxidation with chromic acid gives sebacic acid, nonylene-*α*-dicarboxylic acid (m.p. 124°) and *κ*-ketostearic acid (m.p. 65°).

*λ*-Hydroxystearic Acid,



This acid was obtained (A. Grün and M. Woldenberg, J. Amer. Chem. Soc. 1909, **31**, 490) by the reduction of the methyl ester of ricinoleic acid.

*Sativic Acid*, obtained by oxidising linoleic acid is 8:9:11:12-tetrahydroxystearic acid,



and has been shown to have this constitution (Reinger, Ber. deut. pharm. Ges. 1922, **32**, 124) by progressive elimination of hydroxyl groups, confirming A. Eckert (Monatsh. 1917, **38**, 1).

Four isomeric (*α*-, *β*-, *γ*- and *δ*-) *sativic acids* have been prepared by B. H. Nicolet and H. L. Cox (J. Amer. Chem. Soc. 1922, **44**, 144).

Mild treatment of oleic acid with alkaline permanganate gives *θ*-hydroxy-*ι*-ketostearic acid and *θ*-keto-*ι*-hydroxystearic acid (King, J.C.S. 1936, 1788).

at 0° (E. Bamberger and F. Tschirner, Ber. 1899, **32**, 1675) or electrolytically in acetic acid solution (Haber, Z. Elektrochem. 1898, **5**, 77); by the reduction of nitrobenzene with zinc amalgam in an aqueous-alcoholic solution of aluminium sulphate (E. Bamberger and M. Knecht, Ber. 1896, **29**, 863); or with zinc dust in the presence of calcium chloride in ether or alcohol solution (C. Goldschmidt, *ibid.* 2307; G.P. 84138; see also Wislicenus, J. pr. Chem. 1896, [ii], **54**, 57). The substance is very poisonous and should not be allowed to come in contact with the skin (O. Baudisch, Chem.-Ztg. 1911, **35**, 913).

$\beta$ -Phenylhydroxylamine forms colourless needles, m.p. 81–82°; soluble in 10 parts hot and 50 parts cold water, readily soluble in alcohol, ether, carbon disulphide and chloroform, sparingly soluble in light petroleum. Ammoniacal silver nitrate and Fehling's solution are reduced in the cold by  $\beta$ -phenylhydroxylamine. Mineral acids yield *p*-aminophenol and azoxybenzene; alcoholic sulphuric acid gives azoxybenzene, *o*- and *p*-phenetidine, *o*- and *p*-aminophenol, aniline and other compounds (E. Bamberger and J. Lagutt, *ibid.* 1898, **31**, 1501). It dissolves in sulphuric acid with a deep blue colour. By heating at 100°, azobenzene together with aniline, azoxybenzene and other products are formed. Oxidation with permanganate gives first nitrosobenzene then nitrogen and azoxybenzene (E. Bamberger and F. Tschirner, Ber. 1899, **32**, 342). It dissolves in sodium hydroxide giving a sodium salt, which decomposes into nitrobenzene and azoxybenzene in the presence of air but into azoxybenzene and aniline if air is excluded (E. Bamberger and F. Brady, *ibid.* 1900, **33**, 271). With aromatic aldehydes it yields phenylaldoximes of the type



(G. Plancher and G. Piccinini, Atti. R. Accad. Lincei, 1905, [v], **14**, ii, 36). The 2:4-dinitro-derivative,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{NH}\cdot\text{OH}$ , is made by the action of an alcoholic solution of hydroxylamine on 2:4-dinitrodiphenyl ether. It has marked acidic properties and gives intensely coloured ammonium and aniline salts (W. Borsche, Ber. 1923, **56** [B], 1944).

#### Nitroso- $\beta$ -phenylhydroxylamine,



may be conveniently prepared by the action of sodium nitrite and dilute sulphuric acid on  $\beta$ -phenylhydroxylamine (A. Wohl, *ibid.* 1894, **27**, 1435; E. Bamberger, *ibid.* 1953) or by the interaction of hydroxylamine and nitrobenzene in alcoholic solution in the presence of sodium ethoxide (A. Angeli, *ibid.* 1896, **29**, 1884). It crystallises from light petroleum, m.p. 58–59°, and decomposes at 75°. Readily soluble in organic solvents, sparingly so in water. Alcoholic or ethereal solutions give a brownish-red coloration with a few drops of ferric chloride.

The most important derivative is the ammonium salt, *cupferron*,  $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$ , and is prepared as follows: An ice-cold solution of 25 g. nitrobenzene in 125 c.c., 96% alcohol and

25 c.c. water is saturated with ammonia and then treated with hydrogen sulphide for 2–3 hours. To the resulting pale yellow, pasty mass, 500 c.c. ether are added, the solution shaken vigorously and filtered. The ether layer is separated and saturated with ammonia, withdrawn, cooled in ice and ethyl nitrite vapour passed in ( $\text{NaNO}_2$  25 g.,  $\text{H}_2\text{O}$  40 c.c., 96%  $\text{C}_2\text{H}_5\cdot\text{OH}$  33 c.c. and 1:1  $\text{HCl}$  90 c.c.). The solution becomes dark at first, the colour slowly disappears and crystals of cupferron separate. It is washed with ether and dried over calcium chloride and ammonium carbonate. Yield 80% (K. H. Slotta and K. R. Jacobi, Z. anal. Chem. 1930, **80**, 97). See also Organic Syntheses, 1932, Coll. Vol. I, 171.

The microcrystalline forms of several salts of nitroso- $\beta$ -phenylhydroxylamine have been found to be sufficiently characteristic to be employed in the identification of the particular metal (Martini, Mikrochem. 1928, **6**, 152). Cupferron has been used to separate zirconium and uranium (Angeletti, Gazzetta, 1921, **51**, 285).

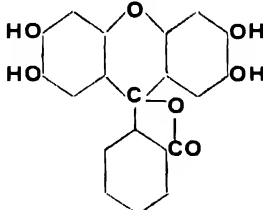
Cupferron is a brownish-white crystalline soluble substance and yields well-defined coordination compounds when its ammonium radical is replaced by many of the metals. It is most useful in the separation of iron, titanium and zirconium, since it precipitates these elements from strongly acid solutions containing aluminium, chromium, manganese, nickel, cobalt, zinc, magnesium and the alkaline earths. The ferric and copper salts may be separated by dissolving out the latter with ammonium hydroxide. The ferric salt is soluble in chloroform, ether, acetone, etc., and may be dissolved and separated from other salts, such as those of lead, silver or tin, which may have been precipitated with it (Baudisch, Chem.-Ztg. 1909, **33**, 1298; 1911, **35**, 913; H. Biltz and O. Hüttke, Z. anorg. Chem. 1910, **66**, 426; J. Hanuš and A. Soukup, *ibid.* 1910, **68**, 52; R. Fresenius, Z. anal. Chem. 1911, **50**, 35). See also CHEMICAL ANALYSIS and Lundell and Knowles, Ind. Eng. Chem. 1920, **12**, 344, for further applications.

#### HYDROXYPROLINE (p. Vol. I, 317c).

**HYDROXYQUINOL**, 1:2:4-trihydroxybenzene. This substance is obtained by rapidly heating hydroquinone with 8–10 times its weight of caustic soda until evolution of hydrogen has almost ceased (Barth and Schreder, Monatsh. 1883, **4**, 176); or by dissolving 150 g. quinone in 400–450 g. acetic anhydride and 10 c.c. concentrated sulphuric acid, keeping the temperature at 40–50°, and finally pouring into much water. The precipitated hydroxyhydroquinone triacetate is saponified with a methyl alcoholic solution of sulphuric acid, neutralised with anhydrous sodium carbonate, extracted with ether, filtered and the solvent removed. The residue is allowed to crystallise in a vacuum desiccator (Thiele, Ber. 1898, **31**, 1248).

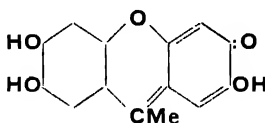
It crystallises from ether in microscopic scales, m.p. 140.5°, and distils with partial decomposition to give quinol. Its aqueous solution darkens rapidly on exposure to the air, and ferric chloride solution gives a transient bluish-green coloration, which changes to dark blue, and then to wine-red on the careful addition of sodium carbonate solution.

Hydroxyquinol (2 mol.) when heated with phthalic anhydride (1 mol.) to 185–190° gives hydroxyquinolphthalein,



(W. Feuerstein and M. Dutoit, *ibid.* 1901, **34**, 2637).

Condensation takes place with aldehydes. Using concentrated sulphuric acid in alcoholic solution, paraldehyde gives the compound :



(C. Liebermann and S. Lindenbaum, *ibid.* 1904, **37**, 1177, 2731).

For an account of the derivatives, see Bargellini (Gazzetta, 1910, **40**, ii, 342; 1911, **41**, ii, 612; 1912, **42**, ii, 351; Atti. R. Accad. Lincei, 1911, [v], **20**, i, 22; ii, 18, 118, 183). The trimethyl ether has been used by J. Reigrodski and J. Tambor (Ber. 1910, **43**, 1964) for the synthesis of 2,3-dihydroxyflavone.

**HYDROXYSTEARIC ACIDS,  $\alpha$ -Hydroxystearic Acid,**



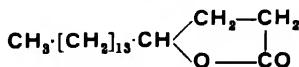
Prepared by treating  $\alpha$ -bromostearic acid with aqueous potash. Separates from a mixture of benzene and light petroleum as a crystalline powder, m.p. 91–92° (C. Hell and J. Sadomsky, Ber. 1891, **24**, 2391; H. R. Le Sueur, J.C.S. 1904, **85**, 827). By heating to 270° it yields margaric aldehyde,  $\text{C}_{16}\text{H}_{33}\text{CHO}$ , a lactide,  $\text{C}_{36}\text{H}_{68}\text{O}_4$ , formic acid and carbon dioxide (Le Sueur, *l.c.*)

$\beta$ -Hydroxystearic Acid,



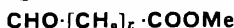
Prepared by treating  $\beta$ -bromostearic acid with aqueous potash. Crystallises from chloroform in white plates, m.p. 89° (Ponzio, Gazzetta, 1905, **35**, ii, 570).

$\gamma$ -Hydroxystearic Acid.—Exists most commonly in the form of its lactone,



which is prepared by heating oleic acid with concentrated sulphuric acid at 80–85° for 6 hours, diluting with water and warming on a water bath; it has m.p. 52–53°, and yields the acid, m.p. 89°, on heating with alkali and finally acidifying with hydrochloric acid (P. W. Clutterbuck, J.C.S. 1924, **125**, 2330).

C. G. Tomecko and R. Adams (J. Amer. Chem. Soc. 1927, **49**, 522) by condensing aldehyde esters of the general formula,



where  $x = 7, 8, 9, 10, 11$  with the Grignard reagent,  $\text{CH}_3 \cdot [\text{CH}_2]_y \cdot \text{MgBr}$  (where  $y = 8, 7, 6, 5, 4$ ) have obtained the esters of the following hydroxystearic acids, from which the pure acids are obtained by hydrolysis,



	M.p., ester.	M.p., methyl ester.
8 or $\theta$ -hydroxystearic acid .	74–75°	45–46°
9 or $\iota$ -hydroxystearic acid .	81–82°	53–54°
10 or $\kappa$ -hydroxystearic acid .	76–77°	49–50°
11 or $\lambda$ -hydroxystearic acid .	78–79°	50–51°
12 or $\mu$ -hydroxystearic acid .	77–77.5°	52–52.5°

$\iota$ -Hydroxystearic acid may also be prepared by the action of sulphuric acid on oleic acid (Tscherbakow and Seizew, J. pr. Chem. 1898, [ii], **57**, 27). At 100° it yields the anhydride, and oxidation with chromic acid in acetic acid converts it into sebacic, azelaic and traces of suberic and a liquid monobasic acid, together with  $\iota$ -ketostearic acid,



m.p. 76°. On distillation,  $\iota$ -hydroxystearic acid gives  $\Delta^4$ -elaidic and  $\Delta^8$ -elaidic acids and ordinary oleic acid (Vesely and Majtl, Chem. Listy, 1925, **19**, 345; Bull. Soc. chim. 1926, [iv], **39**, 230).

$\kappa$ -Hydroxystearic Acid,



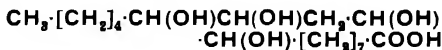
Prepared by the action of sulphuric acid on isocoleic acid, Shukow and Schestakow (J. Russ. Phys. Chem. Soc. 1903, **35**, 1) who give the m.p. as 84–85°. Oxidation with chromic acid gives sebacic acid, nonylene- $\alpha$ -dicarboxylic acid (m.p. 124°) and  $\kappa$ -ketostearic acid (m.p. 65°).

$\lambda$ -Hydroxystearic Acid,



This acid was obtained (A. Grün and M. Woldenberg, J. Amer. Chem. Soc. 1909, **31**, 490) by the reduction of the methyl ester of ricinoleic acid.

*Sativic Acid*, obtained by oxidising linoleic acid is 8:9:11:12-tetrahydroxystearic acid,



and has been shown to have this constitution (Reinger, Ber. deut. pharm. Ges. 1922, **32**, 124) by progressive elimination of hydroxyl groups, confirming A. Eckert (Monatsh. 1917, **38**, 1).

Four isomeric ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -) *sativic acids* have been prepared by B. H. Nicolet and H. L. Cox (J. Amer. Chem. Soc. 1922, **44**, 144).

Mild treatment of oleic acid with alkaline permanganate gives  $\theta$ -hydroxy- $\iota$ -ketostearic acid and  $\theta$ -keto- $\iota$ -hydroxystearic acid (King, J.C.S. 1936, 1788).

***β*-Dihydroxystearic acid** has been prepared by the oxidation of oleic acid with alkali hypobromite at 10–20° in the presence of salts of Ni, Co, Fe and Mn (U.S.P. 2033538).

Hydroxystearic acid from the hydrogenation of castor oil has been used in the form of its salts, Na, K, Ca, triethanolamine, etc., for the preparation of emulsions and creams (Fiero, J. Amer. Pharm. Assoc. 1939, **28**, 598).

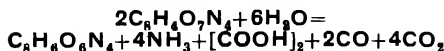
**HYDROZINCITE.** Hydrated basic carbonate of zinc,  $\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2$ , containing Zn 60.5%, of common occurrence as an alteration product of other ores of zinc. It is found in the upper levels of most zinc mines as soft, snow-white encrustations often in stalactitic, botryoidal or other forms. Large masses with an earthy or chalky texture are not uncommon; sp.gr. 3.6–3.8. Much of the material often regarded as smithsonite ( $\text{ZnCO}_3$ ) is really hydrozincite, as shown by its lower degree of hardness (hardness 2–2½, that of smithsonite being 5) and the presence of water. Large quantities have been obtained from the zinc mines of province Santander in Spain, Bleiberg in Carinthia, Sardinia, etc. It has been observed as a mineral of recent formation in the old galleries of lead-zinc mines in North Wales. Analysis of material occurring as minute bladed (monoclinic) crystals at Narlarlar, Western Australia, leads to the formula  $3\text{ZnCO}_3 \cdot 4\text{Zn}(\text{OH})_2$  (R. T. Prider, Min. Mag. 1941, **26**, 60).

L. J. S.

**HYDURILIC ACID**,  $\text{C}_8\text{H}_6\text{O}_6\text{N}_4 \cdot \text{H}_2\text{O}$  or  $2\text{H}_2\text{O}$ ;

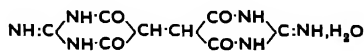


was prepared (1) by Schlieper (Annalen, 1845, **56**, 11), who obtained the acid ammonium salt together with alloxan by the action of nitric acid (sp.gr. 1.25) on uric acid. It is also prepared (2) in the form of its ammonium salt by prolonged boiling of alloxan or alloxantin with very dilute sulphuric acid (Finch, *ibid.* 1864, **132**, 303); (3) by heating crystallised alloxantin under pressure at 170° when it is converted quantitatively into hydurilic acid, according to the equation



or by similarly decomposing alloxan (Murdoch and Doebner, Ber. 1876, **9**, 1102); (4) in the form of its acid ammonium salt by heating dialuric acid with glycerol at 150°, formic acid and carbon dioxide being formed at the same time (Baeyer, Annalen, 1863, **127**, 14; cf. Biltz and Heyn, Ber. 1919, **52** [B], 1298); (5) together with glycine and carbon dioxide by heating uric acid with twice its weight of concentrated sulphuric acid (Schultzen and Filehne, *ibid.* 1868, **1**, 150) (6) by oxidation of barbituric acid in aqueous solution with potassium permanganate (Biltz and Heyn, *l.c.*); (7) by reducing dibromobarbituric acid with hydrogen iodide (Baeyer, Annalen, 1864, **130**, 133); and it is also formed to a small extent (8) by reducing alloxantin with

sulphuretted hydrogen (Murdoch and Doebner, *l.c.*); (9) by the condensation of ethyl ethanetetracarboxylate with urea in the presence of sodium ethoxide at 60–70°, or (10) by the hydrolysis of ethanetetracarboxylguanide



by means of dilute hydrochloric acid at 150° (Conrad, *ibid.* 1907, **365**, 24; cf. Roeder, Ber. 1913, **46**, 2560): whereas ethyl ethanetetracarboxylate and urea yield only a trace of hydurilic acid, *dithiohydurilic acid* is readily obtained from the ester and thiocarbamide; this compound remains unaltered at 250°, and can be desulphurised to hydurilic acid by heating at 100° with concentrated sulphuric acid. Hydurilic acid is most conveniently purified by precipitating the sparingly soluble copper salt from a solution of the neutral ammonium salt, and decomposing this with hot hydrochloric acid, in which the hydurilic acid is only slightly soluble (Baeyer, Annalen, 1863, **127**, 15).

Hydurilic acid crystallises from hot water in small four-sided prisms containing  $2\text{H}_2\text{O}$ , or is precipitated as a fine crystalline powder containing  $1\text{H}_2\text{O}$  by the addition of hydrochloric acid to a hot aqueous solution. It is sparingly soluble in alcohol or cold water, more readily so in hot water; its heat of combustion is 658.5 kg.-cal. (Matignon, Ann. Chim. Phys. 1893, [vi], **28**, 328).

Hydurilic acid bears the same relation to dialuric and barbituric acids that alloxantin bears to alloxan and barbituric acid. Its constitution is established by its synthesis from ethyl ethanetetracarboxylate and urea (*v. supra*), and also by the fact that on hydrolysis with concentrated hydrochloric acid at 200–230° it is converted almost quantitatively into carbon dioxide, ammonia and succinic acid; barbituric acid when similarly treated yields carbon dioxide, ammonia and acetic acid.

Hydurilic acid is not attacked by reducing agents; it yields alloxan and dibromobarbituric acid when treated with bromine water (Biltz, Heyn and Hamburger, Ber. 1916, **49**, 662).

Fuming nitric acid oxidises it into alloxan, whilst weaker acid converts it into nitrobarbituric acid (diluturic acid), isonitrosobarbituric acid (violuric acid) and violantin. Ferric chloride or silver oxide oxidises it to oxyhydurilic acid, which gives a blood-red coloration with ferric chloride. Hydurilic acid has marked acidic properties, and decomposes most metallic chlorides and acetates, yielding the corresponding hydurilate (for the basicity of the acid, see Biltz and Hamburger, *ibid.* 1916, **49**, 655). The heat of neutralisation of hydurilic acid with 2 mol. potassium hydroxide is 21.8 kg.-cal.; but on adding a further quantity of alkali (up to 16 mol.) there is a further evolution of 4.2 kg.-cal., thus pointing to the existence of a third very feeble acid function. The following salts have been described: the *ammonium hydrosulphuric salt*  $\text{NH}_4 \cdot \text{C}_8\text{H}_6\text{O}_6\text{N}_4$ , small octahedra, sparingly soluble, precipitated by acetic acid from solutions of the *normal ammonium salt*  $(\text{NH}_4)_2\text{C}_8\text{H}_6\text{O}_6\text{N}_4$ , which crystallises in needles



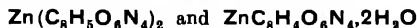
with  $1\text{H}_2\text{O}$  or in large monoclinic crystals with  $4\text{H}_2\text{O}$ ,

$$a:b:c=1.0821:1.0:7.003.$$

Sodium salt  $\text{Na}_3\text{C}_6\text{H}_4\text{O}_6\text{N}_4 \cdot 4\text{H}_2\text{O}$  crystallises in prisms; acid potassium salt  $\text{KC}_6\text{H}_4\text{O}_6\text{N}_4$  forms sparingly soluble microscopic needles; the normal salt  $\text{K}_2\text{C}_6\text{H}_4\text{O}_6\text{N}_4 \cdot 3\text{H}_2\text{O}$  is soluble and crystallises in prisms (Matignon). The calcium salts  $\text{Ca}(\text{C}_6\text{H}_4\text{O}_6\text{N}_4)_2 \cdot 8\text{H}_2\text{O}$  and



are crystalline and almost insoluble; the barium salt  $\text{BaC}_6\text{H}_4\text{O}_6\text{N}_4 \cdot \text{H}_2\text{O}$ ; the zinc salts



are crystalline; the copper salt



forms fine yellow needles or prisms, which become red on heating with loss of water. The silver salt is unstable; the ferric salt is a dark green precipitate, and the formation of a dark green colour with ferric chloride is a characteristic reaction of the salts of hydurilic acid; the ferrous salt is white becoming green; the lead salt is insoluble in acetic acid.

5:5'-Dichlorohydurilic acid,



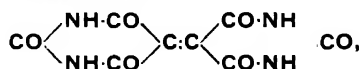
is obtained by the action of potassium chlorate on an intimate mixture of hydurilic and concentrated hydrochloric acids (Baeyer, *Annalen* 1863, 127, 26); a quantitative yield is obtained by chlorinating hydurilic acid in alcohol (Biltz and Hamburger, *l.c.*). It is a sparingly soluble powder, soluble in concentrated sulphuric acid and precipitated therefrom by the addition of water, in small rhombic crystals containing  $2\text{H}_2\text{O}$ ; it is readily decomposed by alkalis yielding the metallic chloride. Hydrolysis to 5-chlorobarbituric acid and alloxan occurs on boiling with water. The potassium salt,  $\text{K}_2\text{C}_6\text{H}_2\text{O}_6\text{N}_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , is a sparingly soluble crystalline powder. The ammonium salt forms hydrated ( $2.5\text{H}_2\text{O}$ ), colourless or pale pink crystals. The anhydrous salt is dark red, m.p. about  $235^\circ$ , becoming discoloured at  $140^\circ$  (Boeck, *Ber.* 1923, 56 [B], 1222).

5:5'-Diethylhydurilic acid is obtained from 5-ethylbarbituric acid by oxidation with potassium permanganate in sulphuric acid. It crystallises with  $1\text{H}_2\text{O}$ , m.p. above  $310^\circ$ . Concentrated potassium hydroxide gradually splits off ammonia; heating with concentrated hydrochloric acid at  $210$ – $240^\circ$  results in hydrolysis to diethyl succinic acid (Aspelund, *J. pr. Chem.* 1933, [ii], 136, 329).

5:5'-Dibenzylhydurilic acid is prepared similarly to the 5:5'-diethyl derivative. It crystallises with  $2\text{H}_2\text{O}$ , m.p.  $315^\circ$  (decomp.) (Aspelund, *l.c.*).

5-Bromo-5'-methoxyhydurilic acid is formed on brominating hydurilic acid in presence of methyl alcohol; it crystallises in stout hexagonal tablets which decompose above  $360^\circ$ ; in presence of ethyl alcohol 5-bromo-5'-ethoxyhydurilic acid is formed which crystal-

lises in stout, elongated prisms decomposing above  $360^\circ$ : these compounds yield 5-methoxyhydurilic acid and 5-ethoxyhydurilic acid on reduction, which lose methyl and ethyl alcohol respectively when heated and yield dehydrohydurilic acid



Biltz, Heyn and Hamburger (*ibid.* 1916, 49, 362; *ibid.* 1919, 52 [B], 1298); cf. Baeyer, *Annalen*, 1863, 127, 26), who found that hydurilic acid broke down under the action of bromine water into dibromobarbituric acid and alloxan.

Tetramethylhydurilic acid (deoxymalic acid),  $\text{C}_{12}\text{H}_{14}\text{O}_6\text{N}_4$ :



is obtained by the dry distillation of amalic acid (Fischer and Reese, *ibid.* 1893, 221, 339), or more conveniently by heating it in a sealed tube for 3 hours at  $180$ – $185^\circ$  (Matignon, *Compt. rend.* 1893, 116, 642); it has also been obtained by heating dimethylpseudouric acid with fused oxalic acid at  $170^\circ$  (Fischer and Ach, *Ber.* 1895, 28, 2473). Deoxymalic acid is crystalline, has m.p.  $260^\circ$ , with decomposition, and can be distilled, although with partial decomposition. It is almost insoluble in hot or cold water; readily soluble in chloroform or acetic acid; its heat of combustion is 1321.8 kg.-cal. (Matignon, *Ann. Chim. Phys.* 1893, [vi], 28, 327). Its chemical properties are similar to those of hydurilic acid; it reduces ammoniacal silver nitrate solution on warming, and gives a beautiful green coloration with ferric chloride; on gentle oxidation it yields a product that gives a blood-red coloration with ferric chloride; but when oxidised by nitric acid it forms dimethylalloxan.

5:5'-Dichlorotetramethylhydurilic acid may be obtained by chlorinating tetramethylhydurilic acid in alcohol; it forms transparent crystals with rectangular section, m.p.  $260^\circ$ . It is devoid of acidic properties, Biltz and Hamburger (*l.c.*).

5-Bromo-5'-methoxy- (or ethoxy-) tetramethylhydurilic acid is formed on brominating tetramethylhydurilic acid in presence of methyl or ethyl alcohol. The bromomethoxy-derivative forms elongated rhombic tablets and has m.p.  $245$ – $247^\circ$  (decomp.) and the bromoethoxy-analogue forms elongated hexagonal tablets, m.p.  $199$ – $200^\circ$  (decomp.).

5:5'-Dibromotetramethylhydurilic acid is formed by the action of bromine on tetramethylhydurilic acid in carbon tetrachloride in complete absence of water; it crystallises in snow-white lancet-shaped leaflets and yields alkyloxy-compounds on treatment with alcohols. It loses both atoms of bromine on heating at  $140$ – $180^\circ$ , forming tetramethyldehydrohydurilic acid, a highly reactive compound which melts at  $284^\circ$ . With boiling methyl alcohol it forms 5-methoxy-tetramethylhydurilic acid which crystallises in stout, four-sided prisms, m.p.  $284^\circ$  (decomp.).

**5-Aminotetramethylhydurilic acid,**

m.p. 295–300° (decomp.) is prepared by acting upon *dehydrotetramethylhydurilic acid* with aqueous ammonia; it crystallises in silky rhombic leaflets. It is reduced by hydriodic acid and phosphonium iodide to 1:3-dimethyluramil, and on bromination in alcohol yields 5:5-dibromo-1:3-dimethylbarbituric acid.

*5-Methylaminotetramethylhydurilic acid* crystallises in rhombic plates.

*5-Anilinetetramethylhydurilic acid* has m.p. 160–161° (decomp.) and forms an aniline salt  $\text{C}_{18}\text{H}_{19}\text{O}_6\text{N}_5\cdot\text{NH}_2\text{Ph}$  which melts at 134°.

Deoxyamalic acid has only two acidic functions; the *potassium*,  $\text{K}_2\text{C}_{12}\text{H}_{12}\text{O}_6\text{N}_4$ , and the *sodium*,  $\text{Na}_2\text{C}_{12}\text{H}_{12}\text{O}_6\text{N}_4$ , salts are sparingly soluble (Matignon, l.c.; Fischer and Ach, l.c.).

For the preparation of *s-dimethylhydurilic acid* and derivatives, see Biltz and Heyn (Ber. 1910, 52 [B], 1298).

M. A. W.

**HYGRIC ACID** (v. Vol. III, 226a).

**HYGRINES** (v. Vol. III, 225d).

**HYDEOXYCHOLIC ACID** (v. Vol. I, 689b).

**HYPACONITINE** (v. Vol. I, 122c).

**HYPAPHORINE** (v. Vol. I, 686d).

**HYPERSTHENE.** A rock-forming mineral belonging to the orthorhombic series of the pyroxene group, and consisting of metasilicate of magnesium and iron ( $\text{Mg,FeSiO}_3$ ). With less iron it passes isomorphously into *bronzeite* and *enstatite* (g.v.). It is a common constituent of basic igneous rocks, especially norite. The very coarse-grained norite found as boulders on the coast of Labrador consists of labradorite (v. FELSAPAR) and hypersthene, the former showing brilliant coloured reflections and the latter a bright coppery sheen. This material is therefore sometimes used as an ornamental or precious stone. The mineral is opaque, with a dingy, brownish-black body-colour, and the metallic reflection is due to the presence of minute crystalline enclosures arranged parallel to one plane. Sp.gr. 3.4.

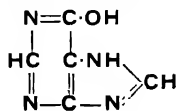
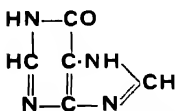
L. J. S.

**"HYPNAL."** Trade name for a compound of chloral and antipyrine which possesses the physiological properties of a mixture of the reactants.

**"HYPNOGEN."** A trade name for diethylbarbituric acid.

**"HYPNONE."** Trade name for acetophenone, a moderately active hypnotic.

**HYPOXANTHINE, Sarcine, 6-Oxypurine.**

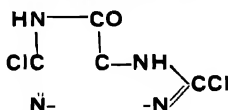


This base was discovered by Scherer (Annalen, 1850, 73, 328) in heart muscle and spleen. Strecker (*ibid.* 1858, 108, 129) isolated a base from the muscles of several animals which he called *sarcine*. It was subsequently shown that sarcine was identical with Scherer's hypoxanthine (see Salkowski, Biochem. Z. 1913, 55,

250; Yoshimura, *ibid.* 1911, 37, 481). Hypoxanthine has been isolated from a very large number of animal and plant tissues. It is, however, easily formed from adenine either *post mortem* or in processes used for its isolation, and there is some doubt as to how much of the base obtained from the tissues represents preformed hypoxanthine. For the isolation from various animal tissues, see also Heymann, Pfüger's Archiv. 1872, 6, 184; Salomon, Z. physiol. Chem. 1878, 2, 72; Ber. 1878, 11, 674; Kossel, Z. physiol. Chem. 1881, 5, 152; 1886, 10, 258; Schindler, *ibid.* 1889, 13, 432; Buglia and Costantino, *ibid.* 1913, 83, 45; Smorodinzew, *ibid.* 1912, 80, 218; Bass, Arch. exp. Path. Pharm. 1914, 76, 40; from urine, Strecker, l.c.; Salomon, Z. physiol. Chem. 1887, 11, 410; Krüger and Salomon, *ibid.* 1898, 24, 385; 1899, 26, 356; and from faeces, Krüger and Schittenhelm, *ibid.* 1902, 35, 158. Hypoxanthine has been found in beer yeast (Schützenberger, Chem. Zentr. 1877, 73), in fungi (Winterstein, Reuter and Korolew, Landw. Versuchs-Stat. 1913, 79-80, 541-562), in hops (Chapman, J.C.S. 1914, 105, 1895), in potato juice (Schulze, Landw. Versuchs-Stat. 1882, 28, 111), in sugar beet (von Lippmann, Ber. 1896, 29, 2645), and in various plants (Schulze and Bosshard, Z. physiol. Chem. 1885, 9, 420). Hypoxanthine has been isolated from steam-heated soils by Schreiner and Lathrop (J. Amer. Chem. Soc. 1912, 34, 1242) and Schreiner and Shorey (J. Biol. Chem. 1910, 8, 385).

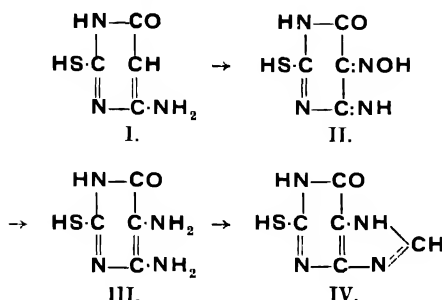
Hypoxanthine is formed in the animal body during the breakdown of nucleic acids. In man adenosine (adenine nucleoside) is first deaminised, forming inosine (hypoxanthine nucleoside) which is then hydrolysed giving hypoxanthine and a pentose (deoxyribose or ribose). In some other mammals enzymes are available which provide an alternative path for the formation of hypoxanthine. Adenosine is first hydrolysed giving adenine (6-aminopurine) and pentose, and the former is then deaminised by the enzyme adenase giving hypoxanthine. The oxidation of hypoxanthine in the body is probably confined to the liver, which contains the necessary enzyme, *xanthine oxidase*, for the conversion of hypoxanthine into xanthine (2:6-dioxypurine) and uric acid (2:6:8-trioxypurine). The latter is excreted by man and the anthropoid ape but most other mammals oxidise it still further to allantoin. For details and literature, see Jones, "Nucleic Acids," Longmans, Green & Co., 1920, or Levene and Bass, "Nucleic Acids" (American Chemical Society Monograph 56), 1931.

The structure of hypoxanthine has been confirmed by syntheses. Fischer (Ber. 1897, 30, 2226; G.P. 17673/1898) by heating trichloropurine with normal aqueous potassium hydroxide obtained 6-*ory*-2:8-dichloropurine,



which he reduced to hypoxanthine by the action of hydrogen iodide. Hypoxanthine was obtained by oxidation of adenine with nitrous acid

(Kossel, Z. physiol. Chem. 1886, 10, 258; Krüger, *ibid.* 1894, 18, 445). It can also be formed by reduction of uric acid with chloroform and alkali (Sundwik, *ibid.* 1897, 23, 476; 1898, 26, 131; 1912, 76, 486). Traube (Annalen, 1904, 331, 64) synthesised hypoxanthine by condensing ethyl cyanacetate and thiocarbamide in the presence of sodium ethoxide. 4-Amino-6-oxy-2-thiopurimidine (I) is formed and gives an isonitroso derivative (II) which yields 4:5-diamino-6-oxy-2-thiopurimidine (III) on reduction.



By heating the sodium salt of the formyl derivative of this compound to 250°, 6-oxy-2-thiopurine (IV) is formed. The sulphur is removed from this compound by heating at 100° with 25% nitric acid yielding hypoxanthine.

Hypoxanthine forms small colourless anhydrous crystals; an unstable hydrated modification has also been observed (Micko, Chem. Zentr. 1904, II, 914). Hypoxanthine decomposes without melting at 150° and dissolves in about 1,400 parts of cold (19°) or 70 parts of boiling water (Fischer, Ber. 1897, 30, 2226). It has both acidic and basic properties, combining with one equivalent of acid or with two equivalents of base. For dissociation constants, see Ogston, J.C.S. 1936, 1713.

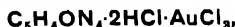
#### Hypoxanthine Hydrochloride,



crystallises in plates or needles; the well-crystallised nitrate,  $\text{C}_5\text{H}_4\text{ON}_4 \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$  is readily soluble in water but sparingly soluble in the presence of nitric acid. Hypoxanthine picrate,  $\text{C}_5\text{H}_4\text{ON}_4 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3 \cdot \text{H}_2\text{O}$ , forms rhombic plates which dissolve in 450–500 parts of water at room temperature (Krüger and Salomon, Z. physiol. Chem. 1898, 26, 362). The phosphotungstate forms straw-coloured plates (Drummond, Biochem. J. 1918, 12, 5). There are two crystalline aurichlorides,



m.p. 240–242° (decomp.), from dilute hydrochloric acid solution and



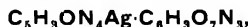
m.p. 259–262° (decomp.), from hot concentrated hydrochloric acid (Hoppe-Seyler and Schmidt, Z. physiol. Chem. 1928, 175, 304). The silver salt,  $\text{C}_5\text{H}_3\text{ON}_4\text{Ag}_2 \cdot \text{H}_2\text{O}$ , loses  $\frac{1}{2}\text{H}_2\text{O}$  at 100°; in the presence of excess of ammonia the compound crystallises in needles

with  $3\text{H}_2\text{O}$  and loses  $2.5\text{H}_2\text{O}$  on drying at 120° for 2 hours (Bruhns, *ibid.* 1890, 14, 544, 566; Krüger and Salomon, *ibid.* 1898, 24, 386).

Some sparingly soluble derivatives formed with salts of metals have been used for the separation and estimation of the base. There is a crystalline mercurichloride,  $\text{C}_5\text{H}_4\text{ON}_4 \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$ , and a compound with silver nitrate,



which crystallises from nitric acid solution. One part of hypoxanthine silver nitrate dissolves in about 4,960 parts of cold nitric acid (sp.gr. 1.1). Hypoxanthine silver picrate,



is precipitated from a hypoxanthine solution by sodium picrate and silver nitrate and forms microscopic lemon-yellow needles insoluble in cold water (Bruhns, *ibid.* 1890, 14, 555).

Hypoxanthine-d-glucoside crystallises in long needles, m.p. 245°, and has  $[\alpha]_D^{20} -34.5^\circ$  in *N*-sodium hydroxide and +12.92° in *N*-hydrochloric acid (Fischer and Helferich, Ber. 1914, 47, 210).

Bromohypoxanthine,  $\text{C}_5\text{H}_3\text{ON}_4\text{Br} \cdot 2\text{H}_2\text{O}$ , is obtained by the action of 1 mol. bromine on 1 mol. hypoxanthine at 120° or by oxidation of bromadenine with sodium nitrite at 70°; it is sparingly soluble in cold water. By heating hypoxanthine with excess of bromine for 6 hours at 100–150° bromohypoxanthinetetrabromide hydrobromide,  $\text{C}_5\text{H}_3\text{ON}_4\text{Br}_4 \cdot \text{HBr}$ , is obtained (Krüger, Z. physiol. Chem. 1894, 18, 449).

#### Hypoxanthine Urethane,



prepared from hypoxanthine and ethylchloro-carbonate, crystallises in sparingly soluble plates, m.p. 185–190° (Bruhns and Kossel, *ibid.* 1892 16, 1).

Hypoxanthine forms a crystalline compound with adenine,  $\text{C}_5\text{H}_4\text{ON}_4 \cdot \text{C}_6\text{H}_5\text{N}_3 \cdot 3\text{H}_2\text{O}$  (Bruhns, Ber. 1890, 23, 225), and through the imino group in position 7 forms coloured derivatives with diazobenzene salts (Burián, *ibid.* 1904, 37, 696).

**Separation and Estimation.**—From mixtures of the purine bases adenine and hypoxanthine can be separated by means of the sparingly soluble compounds with silver nitrate. After removal of silver, adenine is precipitated as the very sparingly soluble picrate, and hypoxanthine is precipitated from the filtrate by addition of ammoniacal silver nitrate (see Bruhns, *ibid.* 1890, 23, 225; Kossel, Z. physiol. Chem. 1883, 8, 404; Schindler, *ibid.* 1889, 13, 432; Krüger, *ibid.* 1894, 20, 170). Hypoxanthine and xanthine can be estimated in blood by oxidation to uric acid by means of xanthine oxidase (Cole, Ellet and Womack, J. Lab. Clin. Med. 1931, 16, 594). For microchemical estimations, see Krebs and Öström, Biochem. J. 1939, 33, 984; Reifer, New Zealand J. Sci. Tech. 1940, 21, 171.

W. V. T.

"HYRGOL." Trade name for a preparation of colloidal mercury (Rosenthaler, Apoth.-Ztg. 1926, 41, 578).

HYSTAZARIN (v. Vol. I, 222c).

## I

**IANTHINITE**.—Hydrous uranous oxide,  $2\text{UO}_3 \cdot 7\text{H}_2\text{O}$ , occurring as velvety crusts of fine needles on pitchblende, of which it is a first alteration product, in the Kasolo mine, Katanga, Belgian Congo, and also at Wölsendorf, Bavaria. The orthorhombic crystals are black with a violet or purple tinge and sub-metallic lustre. Pleochroism is intense—dark violet to colourless. On exposure to air the mineral is altered to greenish-yellow uranic oxide,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , as *berquerelite* or *schoepite* (A. Schoep, *Natuurwetensch. Tijds.* 1926, 7 (for 1925), 97; 1927, 9, 1; *Ann. Soc. Géol. Belgique*, 1927, 49 (for 1926), *Bull.* B188, B310; *Bull. Soc. belge Géol.* 1931, 41, 71; C. Palache, *Amer. Min.* 1934, 19, 313).

L. J. S.

**IANTHONE**,  $\text{C}_{16}\text{H}_{24}\text{O}$ , is a mixture of the two ketones,



b.p. 155–165° and



obtained by the condensation in presence of alkali of mesityl oxide with  $\beta$ - and  $\alpha$ -cyclocitral respectively, *v.* Vol. III, 184b. It is obtained together with ionone when citral and mesityl oxide are condensed in the presence of alkali and the product treated with an acid condensing agent (Durand and Huguenin, *G.P.* 118288). It is a light yellow oil, b.p. 162–172°/15 mm.,  $d_{20}^0$  0.9452,  $n_D^{20}$  ca. 1.5376 (Haarman and Reimer, *G.P.* 127231). When diluted it has a characteristic odour of violets and orris root.

**IBOGAINE**. *Tabernanthe Iboga* Baill., called Iboga or Aboua, grows in the French Congo; it has long been known that extracts from this plant are used as a tonic by the natives. Dybowski and Landrin (*Compt. rend.* 1901, 133, 748) succeeded in isolating a crystalline alkaloid, *ibogaïne*, from Iboga (yield 0.6–1.0%), but it is not quite clear whether this base is responsible for the effect of the Iboga preparation. Almost simultaneously, Haller and Heckel (*ibid.* 1901, 133, 850) found the base *ibogine* in this plant; *ibogine* is probably identical with *ibogaïne*.

*Ibogaïne*,  $\text{C}_{22}\text{H}_{32}\text{O}_3\text{N}_2$  (Dybowski and Landrin) or  $\text{C}_{26}\text{H}_{32}\text{O}_3\text{N}_2$  (Haller and Heckel) has probably the formula  $\text{C}_{20}\text{H}_{28}\text{O}_3\text{N}_2$  (unpublished), colourless prisms, m.p. 149–152° (from abs. EtOH),  $[\alpha]_D^{20}$  –48.5° (in 95% alcohol). The base is soluble in EtOH, Et<sub>2</sub>O, CHCl<sub>3</sub>, acetone and C<sub>6</sub>H<sub>6</sub>, insoluble in H<sub>2</sub>O. The hydrochloride and the picrate (red needles) are crystalline, other salts have not been obtained in crystalline form.

*Ibogaïne* is an indole base, but not a carboline derivative (*see* HARMALINE) (unpublished); it forms salts with one molecule of a monobasic acid. For physiological activity, *see* cited articles and Lambert and Heckel, *Compt. rend.* 1901, 133, 1236; Rothlin and

Raymond-Hamet, *Compt. rend. Soc. Biol.* 1934, 116, 1340.

Schl.

**ICACO** or **Cocoa Plum**. The fruit of *Chrysobalanus icaco* L., a native of Florida, the West Indies and the West Coast of Africa. It resembles a small plum (8 g.) and is used more commonly in the making of preserves than as a dessert fruit. Analytical data recorded by Chace, Tolman and Munson include:

Total solids, 69; protein, 0.46; acids (as malic), 0.13; reducing sugars, 4.1–5.1; sucrose, 0.36; ash, 0.9 (%).

The ash of the pulp contains: K<sub>2</sub>O, 35.15; CaO, 5.84; MgO, 4.51; P<sub>2</sub>O<sub>5</sub>, 3.09; SO<sub>3</sub>, 4.77; and Cl, 18.62%.

A. G. Po.

**ICE COLOURS** (Vol. IV, 227b).

**ICELAND MOSS** (*Cetraria*) is the dried lichen *Cetraria islandica* Linn.

**ICELAND-SPAR** (*v.* Vol. II, 203c).

**ICE-SPAR** (*v.* Vol. III, 440b).

**ICHTHAMMOL** ("ICHTHYOL"). Ichthammol consists chiefly of the ammonium salts of the sulphonic acids prepared from an oily substance obtained by the destructive distillation of bituminous schists, together with ammonium sulphate and water. These schists contain the remains of fish and marine animals, and are found in the Tyrol and on the coasts of the Adriatic, in Switzerland and parts of Italy. The Seefeld district between Southern Bavaria and Tyrol has long been noted for the crude ichthyol. Ichthyol oils from Kashpir shale have been reported (E. V. Rakovskii and S. I. Sokolov, *J. Appl. Chem. U.S.S.R.* 1930, 3, 81).

The oil usually contains about 10% of sulphur. As found in pharmacy, ichthyol contains 5–7% ammonium sulphate, about 50% water, and about 1% of an empyreumatic oil. The British Pharmacopœia lays down standards for the pharmaceutical product.

H. Scheibler has purified the crude oil (*Ber.* 1919, 52 [B], 1903), and has isolated 2-*n*-butylthiophen from oil obtained from Achensee, and 3-*n*-propyl- and 2-isopropylthiophen from Seefeld oil (H. Scheibler and F. Rettig, *ibid.* 1926, 59 [B], 1198; *Arch. Pharm.* 1920, 258, 70).

Ichthyol is soluble in water, partly so in alcohol (90%) and in ether. It is used as a mild antiseptic in skin diseases and also internally. For ichthyolic medicinal preparations, *see* Stadnokov (*Amer. Chem. Abstr.* 1928, 22, 3261). *Bibliography*, U.S. Bur. Mines, Inf. Circ. No. 7042, (1938).

**ICOSANE** (*n*-Eicosane),  $\text{C}_{20}\text{H}_{42}$ ,



The hydrocarbon has been obtained in a high degree of purity from petroleum waxes (C. C. Buchler and G. D. Graves, *Ind. Eng. Chem.* 1927, 19, 718). Synthetically, it may be prepared from *n*-decyl iodide and sodium (Krafft, *Ber.* 1886, 19, 2220), or by reducing eicosyl iodide with zinc and hydrochloric acid (Levene,

West and Van der Scheer, J. Biol. Chem. 1915, 20, 526). Other methods include the reduction of ethyl-*n*-heptadecyl ketone with amalgamated zinc and hydrochloric acid in alcohol (A. Müller and W. B. Saville, J.C.S. 1925, 127, 599) and the reduction of the compound,



with phosphorus and hydriodic acid at 240°C. (Krafft, Ber. 1882, 15, 1717).

Evidence from X-ray diffraction experiments indicates two crystalline modifications of the hydrocarbon (Müller and Saville, *l.c.*; m.p. 36.4°; heat of fusion 14,680 cal./mol. (G. S. Parks and H. M. Huffman, Ind. Eng. Chem. 1931, 23, 1138); b.p. 220°/30 mm. (H. Prophète, Compt. rend. 1926, 183, 609), 205°/15 mm. (K. Ziegler, F. Dersch and H. Wollthan, Annalen, 1934, 511, 13), 148°/0.6 mm. (Levene, West and Van der Scheer, *l.c.*);  $n_D^{25}$  1.4173;  $d_4^{25}$  0.7417 (Buchler and Graves, *l.c.*). For thermal data, see G. S. Parks, H. M. Huffman and S. B. Thomas, J. Amer. Chem. Soc. 1930, 52, 1032.

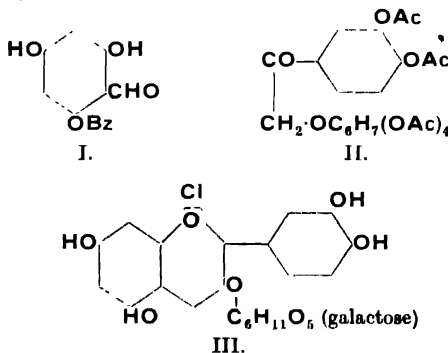
Eicosyl bromide and 1:20-eicosyl dibromide as an unseparated mixture were probably obtained by J. von Braun and E. Kamp (Ber. 1937, 70 [B], 973) from the dicyclohexyl ether of 1:2-eicosylglycol and hydrogen bromide.

"ICYL" COLOURS (v. Vol. IV, 234a).

**IDÆIN.** The orange-red fruits of the cranberry (*Vaccinium vitis-idaea* L.) are coloured with an anthocyanin which is closely related to chrysanthemin and cyanin (*q.v.*), and to which the name idæin has been given (Willstätter and Mallison, Annalen, 1915, 408, 15). The pigment was extracted from the skins of cranberries by means of acetic acid, and after precipitation as the *picrate* was converted into the *chloride* (1.6 g. from 10.7 kg. of skins). G. M. and R. Robinson have obtained the same colouring matter from the leaves of the common beech (*Fagus sylvatica*). An extract of the leaves (collected at the end of May in Oxford) in 1% HCl was saturated with NaCl and the anthocyanin taken up in isoamyl alcohol. Benzene was added, and the pigment re-extracted by means of aqueous HCl. The aqueous solution was thoroughly extracted with ethyl acetate, and then the pigment was transferred to *n*-butyl alcohol after again saturating with NaCl. The alcoholic solution was mixed with light petroleum and the pigment taken up in the minimum volume of 1% HCl. A crude solid pigment was obtained by adding acetic acid and then ether, and repeating the precipitation in the same manner. The *picrate* was prepared, and then the *chloride*, by adding ether to a solution of the *picrate* in methyl-alcoholic HCl. The *chloride* crystallised at once when 5% ethyl alcoholic HCl was added to its concentrated solution in 0.5% aqueous HCl. A *hydrate* of idæin chloride,  $\text{C}_{21}\text{H}_{21}\text{O}_{11}\text{Cl}\cdot 2.5\text{H}_2\text{O}$ , crystallises from 5% HCl when alcohol is added to retard separation. The reddish-brown monoclinic prisms appear brownish-red to grey-violet under the microscope. The powdered salt is reddish-brown and melts with foaming at 210°. The salt becomes anhydrous when kept in a desiccator at the ordinary temperature. In solubility it differs

markedly from cyanin. It dissolves in 10 parts of water at 15° forming a brownish-red solution which becomes orange-red on dilution; *pseudo-base* formation is observed only at high dilutions. It is easily soluble in 0.5% HCl, sparingly in 3% HCl and almost insoluble in 6% HCl. It is rather more soluble in sulphuric acid; 0.03 g. dissolve in 100 c.c. of 7% sulphuric acid at 25°. From this solution characteristic rhombic plates of the *sulphate* crystallise on cooling. The *chloride* is easily soluble in alcohol with a bluish-red colour. The *picrate*, a brownish-red powder which under the microscope is seen to consist of carmine-red needles, dissolves in 30 parts of boiling water but is very sparingly soluble in the cold. Idæin differs from cyanin in that with sodium carbonate or bicarbonate it gives a stable violet colour which is changed to blue only on adding sodium hydroxide. The blue fades to green and finally to yellow. The violet colour is restored when the blue solution is diluted (hydrolysis of the alkali salt of the *colour-base*). Ferric chloride added to the alcoholic solution gives a blue colour, and this becomes violet on diluting. Lead acetate precipitates a blue lead salt from the alcoholic solution. Alum gives a very stable violet colour with the aqueous solution, and bismuth nitrate a reddish-violet colour. The absorption spectrum in 7% sulphuric acid consists of a broad band (green-blue) which resembles that of cyanin but does not extend so far into the blue. The absorption spectrum in the visible region and the alkali colour reactions of idæin resemble those of chrysanthemin very closely, but the behaviour of the two pigments on distribution between amyl alcohol and aqueous acid is quite distinct. Idæin is levorotatory. Hydrolysis by means of aqueous HCl affords cyanidin chloride (1 mol.) and galactose (1 mol.). Its behaviour on distribution between amyl alcohol and aqueous acid is that of a typical monoglucoside.

The structure of idæin has been established by Grove and Robinson (J.C.S. 1931, 2722) who synthesised the colouring matter by condensing 2-O-benzoylphloroglucinaldehyde (I) with  $\omega$ -tetra-acetyl- $\beta$ -galactosidoxo-2:4-diacetoxyacetophenone (II) by means of hydrogen chloride, and obtained an acylated anthocyanin from which idæin chloride (III) was obtained by hydrolysis.



**IDEAL OR PERFECT GAS.—I.** The behaviour of "permanent" gases can be represented by certain empirical laws.

(i) **Boyle's Law.**—At constant temperature the product of the pressure  $p$  and the volume  $V$  of a gas is constant.  $pV = \text{constant}$ . Table I shows how closely this law is obeyed in a number of cases.

TABLE I.

Gas.	$t^{\circ}\text{C.}$	$p$ .	$pv$ .
Helium <sup>1</sup>	0	1.00000	1.00000
		6.01487	1.00228
		8.95584	1.00397
		12.46478	1.00559
Hydrogen <sup>2</sup>	0	1.000	1.0000
		75.795	1.0478
		164.193	1.1078
		442.27	1.3070
Nitrogen <sup>3</sup>	0	1.0000	1.0000
		19.0215	0.99274
		37.9527	0.98730
		52.2158	0.98459

<sup>1</sup> Keesom and van Santen, Comm. Leiden, 1933, No. 227b.

<sup>2</sup> Michels, Nijhoff and Gerver, Ann. Physk. 1932, 12, 502.

<sup>3</sup> Michels, Wouters and De Boer, Physica, 1934, 1, 587.

(ii) **Charles' Law or Gay Lussac's Law.**—This law relates the volume of a gas at constant pressure to the temperature  $t$  of the gas :

$$V_t = V_0(1 + \alpha t)$$

Combining this with (i) it follows that at constant volume

$$p_t = p_0(1 + \alpha t)$$

where  $V_0$  and  $p_0$  are the volume and the pressure of the gas when the temperature  $t$  is zero. The value of  $\alpha$  clearly depends upon the scale on which the temperature is measured. If  $t$  is measured on the Centigrade scale  $\frac{1}{\alpha} = 273.1^{\circ}\text{C.}$

This value is not constant for real gases, and Table II shows values of  $\alpha$  in a number of cases. A more useful scale of temperature can be obtained by setting  $\left(\frac{1}{\alpha} + t\right) = T$ . Making this

substitution  $V_t = V_0 \frac{T}{T_0}$  and  $p_t = p_0 \frac{T}{T_0}$ , where  $T_0 = \frac{1}{\alpha} = 273.1^{\circ}\text{K.}$  When the temperature  $t$  is measured on the Centigrade scale,  $T$  is the absolute temperature (Kelvin scale).

(iii) Laws (i) and (ii) above can be combined to give  $pV = CT$ , where  $C$  is a constant having the value  $C = \frac{p_0 V_0}{T_0}$ . If we take as our standard of quantity 1 mol. then

$$pV = n \frac{p_0 v_0}{T_0} T. \tag{1}$$

where  $n$  is the number of molecules in volume  $V$  and  $v_0$  the molal volume of the gas at pressure  $p_0$ , and temperature  $T_0$ .

TABLE II.

Gas.	$m.$	$p$ Hg.	$\alpha_0 - 100^{\circ} \times 10^7.$	$\beta_0 - 100^{\circ} \times 10^7.$
Helium <sup>4</sup>		0.508		36608.6
		0.750		36607.9
		0.967		36607.3
Krypton <sup>5</sup>		0.862	36,916	
		1.000	36,967	36899.0
Xenon <sup>6</sup>		0.862	37,245	
		1.00	37,395	37202.0

Keesom, van der Horst and Taconis, Comm. Leiden, 1934, No. 230d.

<sup>5</sup> Heuse and Otto, Physikal. Z. 1934, 35, 57.

<sup>6</sup> Heuse and Otto, *ibid.* p. 628.

Heuse and Otto found :—

$$\left. \begin{aligned} \alpha_0 - 100^{\circ} &= 0.0036609 + 358 \times 10^{-7} p \\ \beta_0 - 100^{\circ} &= 0.0036609 + 290 \times 10^{-7} p \end{aligned} \right\} \text{for krypton}$$

and

$$\left. \begin{aligned} \alpha_0 - 100^{\circ} &= 0.0036609 + 785 \times 10^{-7} p \\ \beta_0 - 100^{\circ} &= 0.0036609 + 593 \times 10^{-7} p \end{aligned} \right\} \text{for xenon.}$$

(iv) **Avogadro's Law** states that under the same conditions of pressure and temperature the molal volume of all permanent gases is the same.

Thus the term  $\frac{p_0 v_0}{T_0}$  in equation (1) is a constant applicable to all permanent gases and is called the *gas constant*,  $R$ .

$$pV = nRT.$$

The value of  $R$  can be obtained from a knowledge of the molal volume under some particular experimental conditions, e.g.  $T_0 = 273.1^{\circ}\text{K.}$   $p_0 = 1$  atmosphere,  $v_0 = 22.4$  litres, hence  $R = \frac{22.4 \times 1}{273}$

litre-atm./ $^{\circ}\text{C. mol.}$

**Values of  $R$  in Different Units.**— $R = 1.987$  cal./ $^{\circ}\text{C. mol.}$ ,  $8.314 \times 10^7$  ergs/ $^{\circ}\text{C. mol.}$ ,  $0.08205$  litre-atm./ $^{\circ}\text{C. mol.}$  Gases which obey exactly the law  $pV = nRT$  are known as *ideal or perfect gases*.

Exact obedience to this law over a wide range of temperatures and pressures is not found in practice even with gases which are most difficult to condense. The deviations from the perfect gas law are more marked in the case of gases which are more easily condensed.

**Mixtures of Ideal Gases.**—Dalton's Law of partial pressure states that in a mixture of ideal gases the total pressure  $P$  is the sum of the partial pressures  $p_i$  of the constituent gases.  $P = \sum p_i$ . The partial pressure  $p_i$  of any constituent  $i$  is the pressure which would be exerted by that gas  $i$  if it were present alone with a temperature and volume equal to the temperature and volume of the mixture.

II. THERMODYNAMICS OF A PERFECT GAS.

By definition a perfect gas is one for which the equation of state is

$$pV = nRT.$$

The Energy  $E$  of a Perfect Gas is a function of the temperature only.

In general we have  $\left(\frac{\delta E}{\delta V}\right)_T = T\left(\frac{\delta P}{\delta T}\right)_V - P$ .

But for a perfect gas  $T\left(\frac{\delta P}{\delta T}\right)_V = \frac{nRT}{V} = P$  and hence  $\left(\frac{\delta E}{\delta V}\right)_T = 0$ .

The Heat Content  $H$  of a Perfect Gas is a function of the temperature only.

In general we have  $\left(\frac{\delta H}{\delta P}\right)_T = -T\left(\frac{\delta V}{\delta T}\right)_P + V$ .

But for a perfect gas  $T\left(\frac{\delta V}{\delta T}\right)_P = \frac{n}{P}RT = V$  and hence  $\left(\frac{\delta H}{\delta P}\right)_T = 0$ .

The above two laws mean that for a perfect gas the Joule effect and the Joule-Thomson effect are zero.

In the Joule experiment a gas is expanded adiabatically and without doing any work. This process is in the case of real gases accompanied by a temperature change. Since it is an adiabatic process and no work is done, the process occurs at constant energy content and the effect is measured by  $\left(\frac{\delta T}{\delta V}\right)_E$

$$\left(\frac{\delta T}{\delta V}\right)_E = \frac{P - T\left(\frac{\delta P}{\delta T}\right)_V}{C_V}$$

which is zero for a perfect gas since

$$P - T\left(\frac{\delta P}{\delta T}\right)_V = 0.$$

In the Joule-Thomson experiment the effect is measured by  $\left(\frac{\delta T}{\delta P}\right)_H = \mu$  since no heat exchange occurs during the experiment.

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H = \frac{-V + T\left(\frac{\delta V}{\delta T}\right)_P}{C_P}$$

which is zero for a perfect gas, since

$$-V + T\left(\frac{\delta V}{\delta T}\right)_P = 0.$$

See Table III for values of  $\mu$  for nearly perfect gases.

TABLE III.—JOULE-THOMSON EFFECT FOR NEARLY PERFECT GASES.

$$\mu = \left(\frac{dT}{dP}\right) \text{ in } ^\circ\text{C. per atm.}$$

Helium <sup>7</sup> (pressure 1-200 atm.).

t°C.	-190	-140	-50	0	50	150	300
$\mu$	-0.37	-0.52	-0.59	-0.60	-0.61	-0.62	-0.58

Argon <sup>8</sup> (pressure 1 atm.).

t°C.	-170	-150	-50	0	50	150	300
$\mu$	3.01	1.75	0.58	0.42	0.21	0.18	0.002

<sup>7</sup> Roebuck and Osterberg, Physical Rev. 1933, [II], 43, 60.

<sup>8</sup> *Idem.*, *ibid.* 1934, [II], 46, 785.

The Heat Capacities  $C_V$  and  $C_P$  of a fixed quantity of a perfect gas are dependent only upon the temperature

$$\frac{\delta}{\delta T}\left(\frac{\delta E}{\delta V}\right)_T = \frac{\delta}{\delta V}\left(\frac{\delta E}{\delta T}\right)_V = \left(\frac{\delta c_v}{\delta V}\right)_T = 0$$

$$\frac{\delta}{\delta T}\left(\frac{\delta H}{\delta P}\right)_T = \frac{\delta}{\delta P}\left(\frac{\delta H}{\delta T}\right)_P = \left(\frac{\delta c_p}{\delta P}\right)_T = 0$$

The Relation between the Heat Capacities of a perfect gas

$$\begin{aligned} c_p - c_v &= \left(\frac{\delta H}{\delta T}\right)_P - \left(\frac{\delta E}{\delta T}\right)_V \\ &= \left(\frac{\delta E}{\delta V}\right)_T \left(\frac{\delta V}{\delta T}\right)_P + P\left(\frac{\delta V}{\delta T}\right)_P \end{aligned}$$

But for a perfect gas

$$\left(\frac{\delta E}{\delta V}\right)_T = 0 \text{ and } P\left(\frac{\delta V}{\delta T}\right)_P = nR.$$

Hence  $c_p - c_v = nR$  for  $n$  molecules of gas; or  $C_p - C_v = R$  where  $C_p$  and  $C_v$  are the molal heat capacities.

Compressibilities of a Perfect Gas.—The Isothermal Compressibility  $\kappa$  of a perfect gas

$$\kappa = -\frac{1}{V}\left(\frac{\delta V}{\delta P}\right)_T = \frac{1}{P}.$$

The Adiabatic Compressibility  $\kappa_s$  of a perfect gas

$$\begin{aligned} \kappa_s &= -\frac{1}{V}\left(\frac{\delta V}{\delta P}\right)_s = \frac{C_v}{C_p} \kappa \\ \kappa_s &= \frac{C_v}{C_p} \frac{1}{P} \end{aligned}$$

Equation for Adiabatic Change of a perfect gas

$$\left(\frac{\delta P}{\delta V}\right)_s = \frac{C_p}{C_v} \left(\frac{\delta P}{\delta V}\right)_T = -\gamma \frac{P}{V} \quad \dots (2)$$

where

$$\gamma = \frac{C_p}{C_v}$$

If  $C_p$  and  $C_v$  are independent of temperature (not necessary in the case of a perfect gas, see later) the integration of (2) leads to

$$P \propto V^{-\gamma}$$

$$\text{Value of } \gamma \text{ for a perfect gas: } \gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v}.$$

Ideal Gas—Kinetic Theory Definition.—

On the basis of the Kinetic Theory a perfect gas may be defined as an assembly of atoms or molecules between which there is no energy of interaction and in which the volume occupied by the atoms or molecules is negligible with respect to the total volume of the assembly.

The first of the above conditions means that the whole energy of the assembly is the sum of the kinetic energies of translation and of the rotational, vibrational and electronic energies of the individual molecules. The second condition means that the free volume available for the translational motion of the molecules is equal to the total volume of the whole system. For real gases these conditions are only held over a certain pressure range and as the pressure on the

gas is increased deviations from these ideal conditions will become more serious.

As defined above, the heat capacity of the ideal gas is not necessarily independent of temperature. Some workers have defined a perfect gas not only as one obeying the law  $pV = nRT$  but

also obeying  $\left(\frac{\delta C_v}{\delta T}\right) = 0$ .

In terms of the above model this extra condition limits a perfect gas to an assembly of systems for which quantised changes in the internal energy (rotational, vibrational and electronic) are not allowed. It is, however, sufficient to define an ideal gas as one obeying the law  $pV = nRT$  and this law can be derived statistically or kinetically on the basis of the above conditions of an ideal gas.

M. G. E.

# IDENTIFICATION OF DYES ON TEXTILE FIBRES (v. Vol. IV, 147b-175c).

IDITOL (v. Vol. II, 296d).

IDOCRASE or VESUVIANITE. A mineral consisting of a complex silicate of calcium and aluminium, together with iron, magnesium, water, fluorine, boron, etc. F. W. Clarke's formula is  $R_4Al_2Ca_2Si_6O_{24}$ , where  $R_4 = Ca_2, (AlOH)_2, H_4$ , etc. Crystals are tetragonal and usually green or brown in colour; sp. gr. 3.35-3.45, hardness 6½. The mineral is of common occurrence in contact-metamorphic rocks, particularly crystalline limestones. Lustrous, brown crystals are common at Monte Somma, Vesuvius (hence the name vesuvianite). Green crystals from Ala in Piedmont are cut as gems at Turin. A compact, massive variety, *californite* (Kunz, Amer. J. Sci., 1903, [iv], 16, 397), has been found abundantly as blocks and boulders, measuring up to 6 by 3 feet, at several places in California (Siskiyou, Butte, Fresno and Tulare counties), and is used as a gem-stone and for larger ornamental objects. It is somewhat translucent, takes a high polish, and ranges from bright green to yellowish-green and white in colour, thus closely resembling jade in appearance (D. B. Sterrett, Min. Res. U.S. Geol. Survey, Annual Reports for 1909 and 1910).

L. J. S.

IDRYL (v. Vol. V, 269c).

"IGLODINE." Triiodoethylphenol. An anti-septic (*Iglodine, Newcastle-on-Tyne*).

IGMERALD (v. Vol. IV, 279b; V, 513a).

IGNOTINE (v. Vol. II, 392c).

ILEX VOMITORIA, Aiton. The leaves of this tree, growing in the South Eastern States of America, have been found to contain notable amounts of caffeine; the percentage obtained from ten samples from different localities varied from 1.65 to 0.40 (F. B. Power and V. K. Chesnut, J. Amer. Chem. Soc. 1919, 41, 1307). The leaves are used by the Indians under the name of "Yaupon" as a stimulant.

ILLICLY ALCOHOL (v. Vol. I, 692d).

ILLINIUM. II. At. no. 61; at. wt. 147 (approx.).

J. A. Harris and B. S. Hopkins by fractionally crystallising the magnesium double nitrates of the ceria earths were able to secure a con-

centration of element no. 61 between neodymium and samarium. The amount present was insufficient to make its detection certain by X-ray spectra and attempts to identify it by its absorption bands were complicated by the fact that neodymium and samarium both exhibit broad bands capable of masking those due to no. 61. In separations of these earths made through the bromates, terbium and gadolinium come between no. 61 and neodymium and samarium respectively. Terbium has but one absorption band while gadolinium has none. It thus became possible to observe strong bands at 5830, 5816 and 4520A., and two fainter bands all attributed to element 61; X-ray emission spectra of the samples showing these bands gave lines corresponding with the calculated positions for  $La_1$  and  $L\beta_1$  of no. 61. To the element thus indicated, the name "illinium" was given (J. Amer. Chem. Soc. 1926, 48, 1585, 1594). Rolla and Fernandes (Gazzetta, 1926, 56, 435) claimed priority for the discovery of element 61 to which they gave the name "florentium."

Cork, James and Fogg (Proc. Nat. Acad. Sci. 1926, 12, 696), working on similar lines to Harris and Hopkins, examined the neodymium concentrates from large quantities of monazite sand since such concentrates might be expected to carry most of the illinium. X-ray spectra of the fractions revealed in some of them the I series of element 61, the seven strongest lines being:  $\alpha_2 = 2.289$ ,  $\alpha_1 = 2.279$ ,  $\beta_1 = 2.078$ ,  $\beta_2 = 2.038$ ,  $\beta_3 = 1.952$ ,  $\gamma_1 = 1.799$ ,  $\gamma_2 = 1.725$ . The amount of illinium oxalate estimated as being present in the fractions was from 1-1.5%.

Determinations of the basicity of the element by fractional precipitation with sodium nitrite places it after neodymium and before yttrium in the series Pr, Nd, II, Y, Sm (Hughes and Hopkins, J. Amer. Chem. Soc. 1933, 55, 3121).

In spite of all the foregoing work illinium does not yet figure in international tables of atomic weights and it is doubtful if the salts have been obtained sufficiently pure to establish definitely the individuality of the element. Indeed, Jensen (Naturwiss. 1938, 26, 381) has suggested reasons for questioning whether element no. 61 can exist as a stable nucleus.

G. R. D.

ILLIPÉ BUTTER (v. Vol. I, 653c).

ILLIPÉ NUTS (v. Vol. II, 31d, 32a).

ILLIPENE (v. Vol. I, 653d).

ILLURIC ACID (v. Vol. III, 338b).

ILLURIN BALSAM (v. Vol. III, 338b).

ILMENITE, or Titaniferous Iron-Ore. A common mineral with approximately the formula  $FeTiO_3$ , but of variable composition. Analyses show  $TiO_2$  22-59,  $FeO$  20-46,  $Fe_2O_3$  1-59%. In its rhombohedral crystalline form it shows a close agreement with hematite, and it has consequently, until recently, been regarded as an isomorphous mixture of ferric oxide and titanium sesquioxide, the formula being written as an oxide  $(Fe,Ti)_2O_3$ . The discovery of the rhombohedral titanates of magnesium and manganese, *geikielite* ( $MgTiO_3$ ) and *pyrophanite* ( $MnTiO_3$ ), and the frequent presence of magnesium (and manganese) in ilmenite, suggest, however, that the mineral is really a titanate of ferrous iron,  $FeTiO_3$  (S. L. Penfield, Amer. J.



Sci. 1897, [iv], 4, 108). In the variety *pyro-ilmenite* a considerable amount of iron is replaced by magnesium, the formula then being  $(\text{Fe}, \text{Mg})\text{TiO}_3$  (T. Crook and B. M. Jones, Min. Mag. 1906, 14, 105).

Ilmenite is black with a sub-metallic lustre, and often a smooth and lustrous conchoidal fracture, sp.gr. 4.5-5; hardness 5-6. The massive mineral somewhat resembles magnetite in appearance, from which it is readily distinguished by its feeble magnetic character. It is of constant occurrence as isolated grains in the more basic igneous rocks (gabbro, diabase, basalt, etc.); and in certain instances it forms rich segregations in such rocks. Enormous deposits of ilmenite are found under these conditions at several places in Norway, Sweden, Canada and the United States. With the weathering and breaking down of these igneous rocks, grains of ilmenite (*manaccanite*, from Manaccan in Cornwall) collect in the beds of streams and on the sea-shore, sometimes forming considerable deposits of "black iron-sand."

Although large deposits of ilmenite are available for mining, the mineral has not yet found any important applications. It has been used for the preparation of titanium paints and enamels; and in the future it may be more utilised for the manufacture of titanium-steel, which possesses great ductility and a high limit of elasticity. (See J. T. Singewald, The Titanium-ferous Iron Ores of the United States, their Composition and Economic Value, U.S. Bureau of Mines, 1913, Bull. 64.)

L. J. S.

**ILVAITE**, Lievrite or Yenite. Acid silicate of iron and calcium,



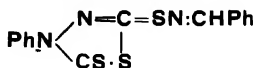
crystallised in the orthorhombic system. It contains theoretically  $\text{FeO}$  35.2,  $\text{Fe}_2\text{O}_3$  19.6% (Fe 41%), but the ferrous oxide is partly replaced by an equivalent amount of manganese oxide (up to 8.6%). Sp.gr. 3.9-4.1, hardness 5½-6; gelatinises with hydrochloric acid. The mineral is found somewhat abundantly as brilliant black crystals and as compact masses in the iron mines at Rio Marina and Cape Calamita in Elba. It is also known from Campiglia Marittima in Tuscany, Hebron in Nassau, British Columbia, Greenland and Japan.

L. J. S.

**IMIDES** (v. Vol. II, 371a, 375c).

**IMINES**. The imines are compounds in which the oxygen atom of a carbonyl group is replaced by  $\text{NH}$ , thus forming aldimines and ketimines from aldehydes and ketones respectively. Ketimines are often termed ketimides in the literature.

The substituted aldimines are known as Schiff's bases, but the unsubstituted aldimines have been isolated in a few cases only. Busch (Ber. 1896, 29, 2136) isolated benzaldimine hydrochloride,  $\text{C}_6\text{H}_5\text{CH}:\text{NH}\cdot\text{HCl}$ , by treating a benzene solution of the compound



with hydrogen chloride; also (*idem. ibid.* 1896, 29, 2144) by adding a saturated alcoholic solution of hydrogen chloride to hydrobenzamide in dry benzene at 5°C.

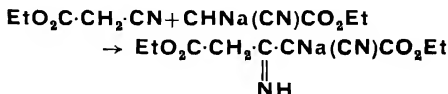
A. Hantzsch and F. Kraft (*ibid.* 1891, 24, 3517) obtained the ketimine of benzophenone by converting the ketone to the dichloro-compound, and treating this with urethane to obtain



which was decomposed by hydrogen chloride to give the ketimine hydrochloride. To obtain the base they passed dry ammonia into a chloroform solution of the hydrochloride, filtered from the precipitated ammonium chloride and removed the chloroform *in vacuo*.

*Iminoacetoacetic ester* may be prepared by the action of ammonia upon acetoacetic ester. The ketimine is tautomeric with  $\beta$ -aminoacrylic acid ester. See K. von Auwers *et al.*, on ketimine-enamine tautomerism (*ibid.* 1930, 63 [B], 1072; 1931, 64 [B], 2758).

J. F. Thorpe and his colleagues investigated reactions of the type



(Thorpe, Baron and Remfry, J.C.S. 1904, 85, 1726).

For a summary of the Thorpe reactions, see Linstead, *ibid.* 1941, 453.

Trichloroacetonitrile, in the presence of aluminium chloride, condenses with toluene, mesitylene, tetraline, phenol, 1:4:5-xyleneol, 3:5-dimethylanisole, thymol and carvacrol to give the corresponding ketimines (J. Houben and W. Fischer, Ber. 1930, 63 [B], 2455).

G. Mignonac (Chem. Zentr. 1935, I, 1201) attempted to prepare the aldimine by catalytic reduction of the nitrile or oxime and by dehydrogenation of the amine, but was unable to isolate the free base; he was more successful in the preparation of ketimines, e.g. phenylnaphthylketoxime gave phenylnaphthylketimine, m.p. 68-69°C.

Substituted ketimines may be prepared from the ketone and the sodioamine (U.S.P. 1938890; Chem. Zentr. 1934, I, 3801).

"**IMOGEN**," "*Eikonogen*" (*q.v.*) modified by the introduction of a second amino-group; used as a photographic developer.

**IMOGEN SULPHITE** was an Agfa preparation said to consist of eikonogen mixed with sodium sulphite.

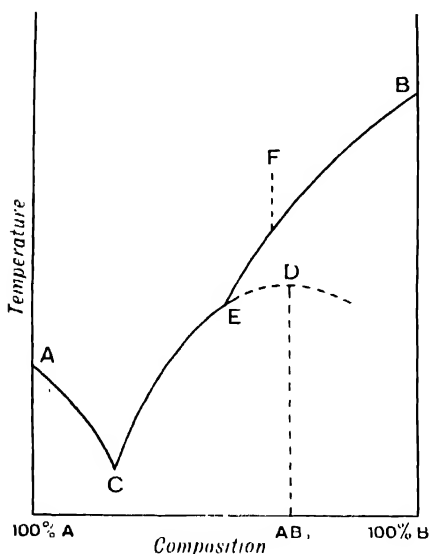
**IMPERIALINE** (v. Vol. V, 330a).

**INCARNATRIN** (v. Vol. III, 245a).

**INCONGRUENT MELTING-POINT.**

—When two substances A and B form a compound of the general type  $\text{A}_x\text{B}_y$  which, however, is so unstable that it decomposes completely at a temperature below its melting-point, the phase-equilibrium diagram for the system is that shown in the figure; the compound as illustrated in this case is a 1:2 compound  $\text{AB}_2$ . This diagram refers to the "condensed" system, i.e. only solid and liquid phases are considered. A and

B represent the melting points of the pure substances A and B respectively, and C represents the eutectic, the temperature below which no liquid phase can exist. At a temperature E below its hypothetical melting-point D, the compound  $AB_2$  dissociates completely into liquid and the pure component B. The point E is called the *incongruent melting-point of the compound*. It differs from a *true melting-point* in that the solid and liquid phases in equilibrium with one another at this temperature are of different composition. At the point E the condensed system is invariant, *i.e.* the temperature of E is fixed, since there are two solid phases,  $AB_2$  and pure B, and one liquid phase in equilibrium. Hence if a liquid of composition F is cooled, the solid which separates first is B, and when the temperature falls to E, formation of the solid  $AB_2$  begins. The



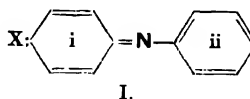
temperature then remains constant at E until one of the phases (either solid B or the liquid phase, depending on whether F is to the left or the right of D) disappears, yielding either solid  $AB_2$  + liquid or solid B + solid  $AB_2$ . This arrest in the cooling curve at the incongruent melting-point is very similar to the phenomenon observed at the transition point when a substance exists in two enantiotropic forms (*i.e.* two modifications each of which is stable over a certain range of temperature and pressure and which undergo reversible transformation of one into the other under fixed conditions of temperature and pressure). For this reason the point E is frequently referred to as a transition point. The two cases can, of course, easily be distinguished by an examination of the solid phases.

For m.p.-composition diagrams of other binary mixtures and compounds, see Vol V, 242d, 250c.

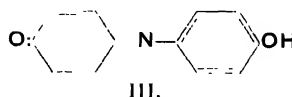
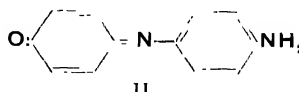
G. C. H.

INDACONITINE (v. Vol. I, 122d).

**INDAMINES and INDOPHENOLS** are coloured compounds containing the chromophore system (I) where X is either NH or O :

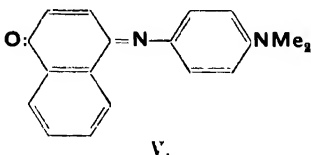
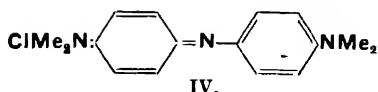


In the specific instance (I), the colour is assumed to be due to resonance between the molecular structure as depicted and alternative structures involving ring (ii) in a quinonoid system (Bury, J. Amer. Chem. Soc. 1935, 57, 2115). The dyestuffs of this group, usually blue-green to violet in colour, contain at least one basic auxochromic group in *o*- or *p*-positions in ring (ii) so that "normal" indophenols (or more precisely "indoanilines") (II) and "acid" indophenols (III) which are wholly phenolic in nature may be envisaged.



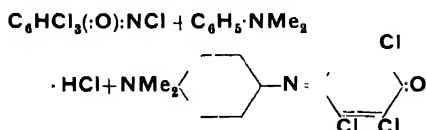
*Historical.*—Although an impure indamine had been obtained as an intermediate in the preparation of safranine and probably even earlier by oxidation of aniline alone, the first pure preparation was achieved by Witt (Ber. 1879, 12, 931; J.C.S. 1899, 75, 356) by the interaction of the hydrochloride of *p*-nitrosodimethylaniline and *m*-toluylenediamine. The first representatives of the "acid" indophenols were obtained by Hirsch (Ber. 1880, 13, 1909) by the condensation of quinone chlorimide with phenols in concentrated sulphuric acid (*cf. also* Möhlau, *ibid.* 1883, 16, 2845). Owing to their fugitiveness towards acids indophenols are of little value as dyestuffs, but commercial indophenol (*v. infra*) and others of its class may be applied as vat dyes as they readily yield leuco-derivatives (substituted diphenylamines) and, moreover, yield with indigo a mixture which simulates in many respects indigo itself—owing, probably, to chemical association of the two dyestuffs. This vat blue has now, however, been largely replaced by synthetic indigo and sulphur colours; many of the latter are directly obtained from indophenols which have thus assumed some renewed importance. Indophenols are also of value as intermediates in the dye industry. They also afford a ready source of diphenylamine derivatives.

*Preparation.*—(a) By condensing nitrosoamines or nitrosophenols (quinone oximes) with amines or phenols. Thus *p*-nitrosodimethylaniline affords with dimethylaniline *Bindschedler's Green* (IV) or with *α*-naphthol *Indophenol Blue* (V).

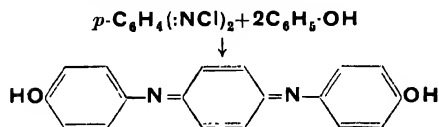


(b) Indophenols and indamines are obtained by oxidising mixtures of *p*-diamines or *p*-aminophenols with bases containing a free position *para* to the basic group; suitable oxidising agents are manganese dioxide or lead peroxide (Nietzki, *ibid.* 1895, **28**, 2969) or potassium chromate or dichromate in neutral or acid solution. In this way aniline and *p*-phenylenediamine yield the simplest indamine, *Phenylene Blue* (*v. infra*).

(c) Many indamines and indophenols are obtainable by processes recalling (b) but in which the oxidation has been effected prior to condensation. Thus quinonechloroimides and aromatic bases yield indophenols:



whilst "acid" indophenols are formed when the second component is a phenol. Dichloroimides react with phenols to give more complex indophenols in which three nuclei may be regarded as comprising the chromophore:



Indophenols of these simple types are often formed as intermediates in the production of phenazine, oxazine and thiazine dyestuffs (*cf.* Eichler, *Monatsh.* 1937, **70**, 73), and others such as carbazole indophenol (*v. infra*) have found particular application in the manufacture of sulphur colours.

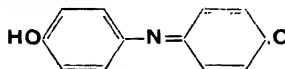
**Properties.**—Most indophenols are blue or green in colour, their simple salts being soluble in water. Such solutions have little direct affinity for vegetable fibres and their limited direct application is due to their ability to take up two atoms of hydrogen with formation of leuco-compounds which may be re-oxidised to the dyestuff. Indophenol itself has been used in this way in association with indigo. These dyeings are fugitive to acids as indophenols readily undergo fission into *p*-quinones and thus their more important application lies in their further conversion into sulphur colours. Occasionally it is advantageous to synthesise the leuco-compound and subsequently oxidise it;

Vol. VI.—27

thus the product of the reaction between *m*-toluylenediamine and formaldehyde bisulphite compound is condensed with *p*-nitrosophenol and finally oxidised and the indophenol heated with sulphur and sodium sulphide to give Thionol Purple (B.P. 24008, 1906). The readiness with which indophenols are reduced makes them valuable indicators in the determination of oxidation-reduction potentials, particularly in bacteriological and other biological systems (*see* L. F. Hewitt, "Oxidation-Reduction Potentials in Bacteriology and Biochemistry," 2nd ed., London, 1933).

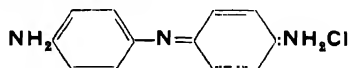
The following account includes the more important commercial dyestuffs and intermediates of this type:

#### *Phenol indophenol*

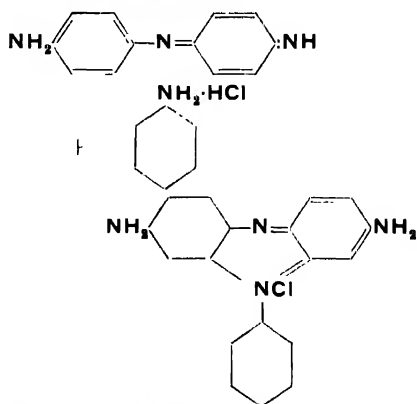


is of no direct importance but on treatment with sulphur and sodium sulphide yields a fast dye resembling indigo (Fierz-David, "Kunstliche organische Farbstoffe," J. Springer, Berlin, 1933).

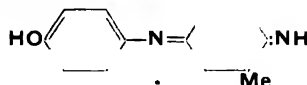
#### *Aniline indoaniline*



*Phenylene Blue*, is prepared by oxidising an equimolecular mixture of *p*-phenylenediamine and aniline hydrochloride with cold aq. potassium dichromate (Nietzki, "Chemie der organischen Farbstoffe," 5th ed., Berlin, 1906, p. 200). The hydrochloride crystallises in green needles which dissolve in water to a greenish-blue solution. In acid solution *Phenylene Blue* is moderately rapidly hydrolysed to benzoquinone and possesses therefore little stability. It is converted by boiling with aniline hydrochloride solution into *Phenosafranine*:



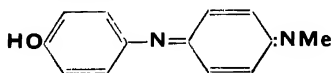
#### *Phenol indo-o-toluidine*



produced by direct condensation of *o*-toluidine

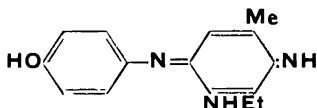
with *p*-nitrosophenol (U.S.P. 727387), is the source, after fusion with sodium sulphide and sulphur of the cotton dyestuff *Thionol Blue*.

*Phenol indomethylaniline*,



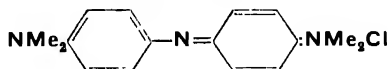
is, after sulphonation, converted into an indigo-like dye by fusion with sulphur and sodium sulphide (G.P. 129024, 129325).

*Phenol indo-4-ethylamino-o-toluidine*,



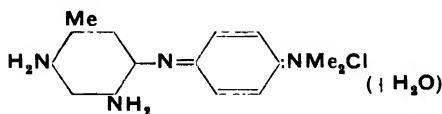
yields on fusion with sulphur a bright purple dyestuff of value in dyeing and printing cotton (U.S.P. 829740).

*Tetramethylphenylene Blue*,



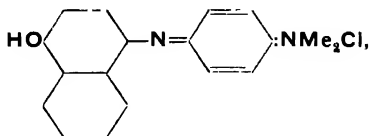
*Bindscheller's Green* (Bindscheller, Ber. 1880, 13, 208; 1883, 16, 865), is obtained by condensing *p*-nitrosodimethylaniline with dimethylaniline (*cf. also* Wieland, *ibid.* 1915, 48, 1087). The commercial dyestuff usually consists of its double salt with zinc chloride.

*Tolylene Blue*,



is formed on oxidising *p*-dimethylaminoaniline and *m*-tolylenediamine (Witt, Ber. 1879, 12, 931; G.P. 15272). The monohydrochloride crystallises in bronze-coloured crystals.

*α-Naphthol Blue*,

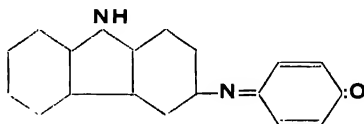


is prepared commercially by reducing *p*-nitroso dimethylaniline and condensing the resulting amino-compound with *α*-naphthol in warm caustic alkali, finally oxidising the leuco-compound at 0° to +2° with sodium hypochlorite (Witt, J.S.C.I. 1882, 1, 255; G.P. 15915, 18903, 19231). The free dye, which separates as a dark brown powder, is almost invariably applied as a vat dyestuff (*e.g.* in cotton printing) and hence is found on the market as the tin salt of its leuco-compound (*Indophenol White*). It is still more frequently used as a vat mixture with indigo, but its most important use lies in the production of the sulphur colour *Thio-phorindigo*.

An ill-defined indamine used for the preparation of coloured lakes and cheap coloured papers, etc., is obtained by oxidising 1:2-naphthalenediamine sulphonic acids (G.P. 224442) which contain halogen in the 8-position (G.P. 431943) with ferric salts. These yield particularly bright shades of green on incorporating yellow azo-dyestuffs.

The indophenol obtained from *p*-nitrosophenol and *α*-naphthylamine is the source of *Suldura Green*.

*Carbazole indophenol*,

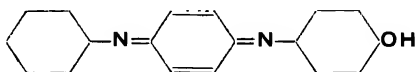


is the dye obtained by condensing *p*-nitrosophenol with carbazole in concentrated sulphuric acid at > 30° (G.P. 230119; U.S.P. 919572, 931598, 1465853) or by oxidising carbazole and *p*-aminophenol in sulphuric acid with manganese dioxide.

Carbazole Indophenol forms a dark violet powder, insoluble in water, and is the source of sulphur colours (G.P. 218371) such as *Hydro Blue R* (U.S.P. 956348). The corresponding chloroindophenols derived from chlorocarbazoles or chloro-*p*-nitrosophenols are claimed to yield sulphur colours faster to bleaching (G.P. 235364).

The corresponding halogeno-*N*-ethylcarbazole indophenol is prepared similarly and converted by boiling with sulphur and sodium sulphide in alcohol into *Sulphanthrene Blue G* (G.P. 222640, 235364). Similar products from benz- and naphtho-carbazoles and nitroso-phenols or -cresols have also been described (F.P. 818684).

The sulphur colours obtained from the complex indophenol,



prepared from *p*-nitrosophenol and diphenylamine at -20°, is the subject of patent claims (U.S.P. 1777757). More complex compounds of the type

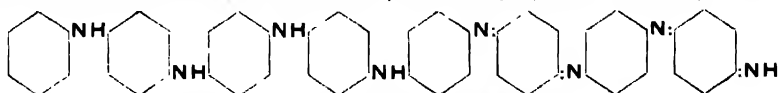


where R' = H or alkyl and R = alkyl or cycloalkyl yield greenish-blue sulphur colours (B.P. 467920).

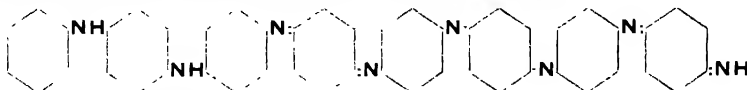
Another type of indophenol is obtained by replacing the hydroxyl group in a 6- or 8-arylamino-2-hydroxy-3-naphthoic acid by an indophenol residue, followed by loss of carbon dioxide and oxidation of the leuco-compound (B.P. 334700).

In addition to the above well characterised indophenols more drastic oxidation of aromatic bases containing a free position *p*- to the amino-residue gives rise to still more complex structures which may be regarded however as containing the indophenol chromophoric nucleus.

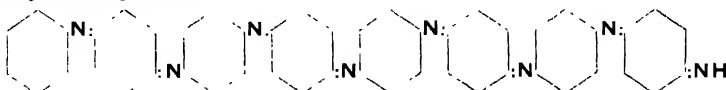
Thus oxidation of aniline with chloric acid in presence of vanadium salts affords the octa-



Emeraldine is further oxidised by hydrogen peroxide to *Nigraniline* :

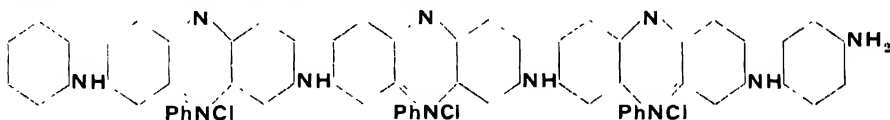


and finally to *Pernigraniline* :



In accordance with the proposed quinoneimine structure (*Literature* : See Schultz, Farbstoff-Tabellen, 7th ed., I, 619) these are unstable towards acids, and for the stable Aniline Black

a structure is assumed in which alternate imine residues have become members of phenazine systems :

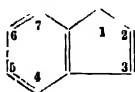


**INDANTHRENE COLOURS** (v. Vol. I, 414-427).

**INDANTHRONE** (v. Vol. I, 411d, 414d).

**INDAZINE** (v. Vol. I, 577c).

**INDENE, C<sub>9</sub>H<sub>8</sub>**

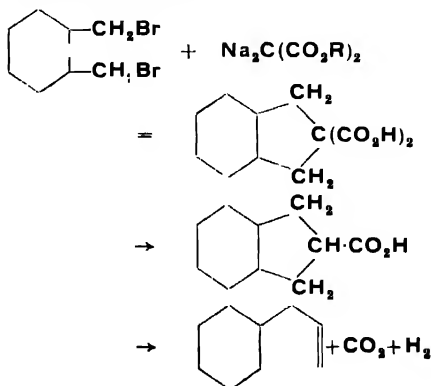


is a liquid hydrocarbon of growing industrial importance. It occurs as a constituent of coal-tar naphtha, being contained chiefly in the fraction of b.p. 175-185°, and in derived products such as coal gas and carburetted water-gas (Dennstedt and Ahrens, Ber. 1894, 127, 602) which may contain as much as 100 g. of indene in 1,000 cu. ft. (Ward, Jordan and Fulweiler, Ind. Eng. Chem. 1932, 24, 969, 1236; 1934, 26, 947, 1028). Being produced by pyrolytic decomposition of carbonaceous material indene is found less abundantly in low-temperature carbonisation distillates (Weissgerber, Brennstoff-Chem. 1924, 5, 208; Ber. 1928, 61 [B], 2111), but on the other hand is formed in considerable amount by pyrolysing mixtures of acetylene and hydrogen (R. and W. Meyer, *ibid.* 1918, 51, 1571) or natural gas (Birch and Hague, Ind. Eng. Chem. 1934, 26, 1008).

The isolation of indene was first effected by fractionating higher-boiling portions of coal-tar light oil (Krämer and Spilker, Ber. 1890, 23, 3276) and converting the enriched mixture into picrates. On distilling the picrates in steam, those of naphthalene and coumarone are unaffected whilst indene picrate is broken down and indene is recovered from the distillate (*cf.* Orlov, Protjanowa and Flegontow, Chem. Zentr. 1937, I, 3435). Although 3 g. of crude indene were obtained from 10 g. of naphtha the method is unsatisfactory and even dangerous because of

the explosive nature of the picrates. One hydrogen atom of indene is however replaceable by sodium by treating with the metal, preferably in presence of ammonia or other bases such as pyridine or aniline (G.P. 209694, 205465), and Weissgerber has utilised this reaction to isolate indene by distilling off unreacted material and then decomposing the indene sodio-compound with water (Ber. 1909, 42, 569; *cf.* Courtot and Dondelinger, Ann. Chim. 1925, [x], 4, 231). More recently, processes consisting in freezing indene out of naphtha fractions containing 80% indene at -25° have formed the subject of patent claims (U.S.P. 1943078; R.P. 405900).

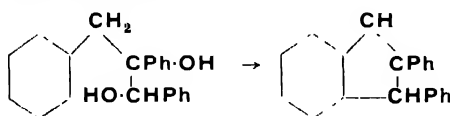
The structure of indene is indicated by its unsaturated character, *e.g.* towards bromine, and by the formation of phthalic acid by oxidising with 30% nitric acid (Krämer and Spilker, *loc. cit.*), and a number of syntheses such as the following (von Baeyer and Perkin, Ber. 1884, 17, 125; *cf.* Kipping and Hall, *ibid.* 1900, 77, 469) confirm this structure :



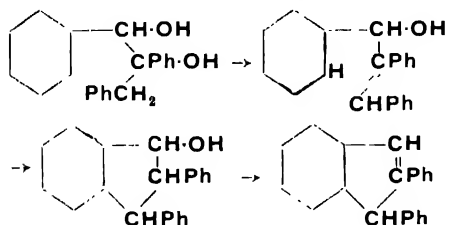
Indene is also available synthetically from its derivatives such as  $\alpha$ -hydrindone. Raman spectra indicate (Matsuno and Han, Bull. Chem. Soc. Japan, 1936, 11, 321) that indene is a resonance hybrid of the two structures:



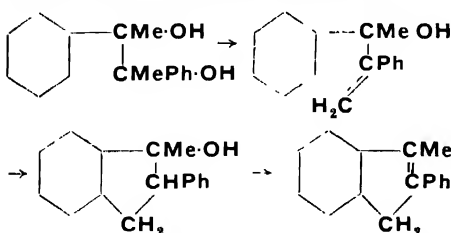
A recent synthesis of the indene nucleus which is of extended application consists in dehydrating suitable pinacones, e.g.  $\alpha$ -benzyl hydrobenzoin, with acetyl chloride or phosphorus pentoxide to yield 1:2-diarylundenes. Orékhoff and Tiffeneau (Bull. Soc. chim. 1922, [iv], 31, 253) formulated the reaction as a simple dehydration between one of the pinacone hydroxyl groups and a hydrogen atom attached to one of the aromatic residues:



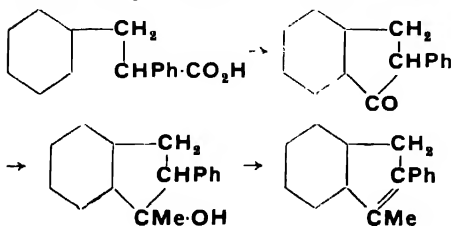
Blum-Bergmann on the other hand suggested (Ber. 1932, 65 [B], 109) the alternative scheme:



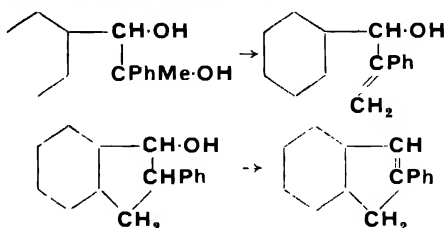
on the evidence that the change is not exclusive to benzyl pinacones but can also take place with fatty-aromatic pinacones. Thus the product of dehydrating acetophenone pinacone, although previously regarded as 9:10-dimethylanthracene, was identified as 2-phenyl-3-methylindene:



The last was synthesised by the classical method:

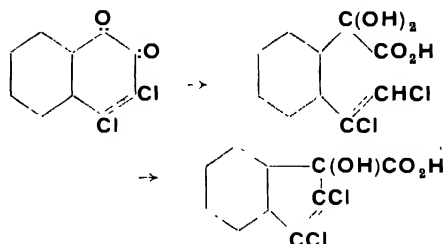


Again, the simpler  $\alpha$ -methylhydrobenzoin is now known to yield on dehydration not a hydrocarbon,  $C_{30}H_{22}$ , as formerly supposed, but 2-phenylindene,  $C_{15}H_{12}$ :



It should be mentioned that the reaction is not a general one and Blum-Bergmann states that  $\alpha$ -methylhydrobenzoin and benzylhydroanisoin and other aromatic pinacones do not yield indene derivatives.

The formation of indene derivatives (Zincke and co-workers, *ibid.* 1886, 19, 2500; 1887, 20, 1265, 2894, 3216; 1888, 21, 491, 2381, 2379; 1894, 27, 744; Annalen, 1892, 267, 319; 1894, 283, 341; 1898, 300, 197) by the rearrangement of naphthalene compounds containing strongly negative substituents is of some interest, e.g.:



The purified hydrocarbon  $C_{10}H_{10}$  from the coal-tar naphtha, b.p. 200–210°, yielded on oxidation a mixture of trimellitic and hemimellitic acids indicating the probable presence of the four possible methylindenes in the hydrocarbon mixture (Bocs, Ber. 1902, 35, 1762).

**Physical Properties.**—Indene is a colourless mobile oil, b.p. 182°, m.p.  $-2^\circ$ ; this comparatively high melting-point, together with a high molecular depression (7.28°) make indene a convenient solvent in cryoscopic determinations of molecular weight (Klatt, Z. physikal. Chem. 1934, 171, 454). Indene readily polymerises not only by chemical reactions (*cf. infra*) but also by the action of light, heat and high pressure (U.S.P. 1952116). Polymerisation by exposure to sunlight or ultra-violet light (Guntz and Minguin, Compt. rend. 1911, 152, 373; Ciamician and Silber, Ber. 1913, 46, 420; Weger and Billmann, *ibid.* 1903, 36, 642) can proceed in absence of other catalysts but is favoured by the presence of air. Thermal rearrangements with polymerisation giving rise to truxene, chrysene, etc., have also been described.

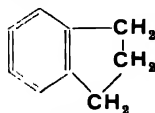
**Chemical Properties.**—The following reactions of indene are important:

(a) Those in which the double bond in the 5-membered ring functions as an olefinic linking.

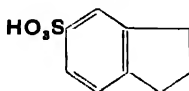
(b) Reactions in which the aromatic ring is substituted.

(c) Reactions of aliphatic character involving the methylene group.

(a) Indene exhibits many of the properties of an olefin. Thus relatively mild reduction (Cook and Linstead, J.C.S. 1934, 946) affords the more stable compound *indane* (*hydrindene*). Indane possesses most of the aromatic properties of



Indane.



Indane-5-sulphonic acid.

indene but the 5-membered ring is practically devoid of the reactivity it exhibits in indene itself. Thus indane may be sulphonated to yield the readily crystallisable 5-sulphonic acid (Cook and Linstead, *l.c.*) and nitrated to a mixture of 4- and 5-nitroindanes which are themselves reducible to aromatic bases (Braun, Arkuszewski and Köhler, Ber. 1918, 51, 291). More drastic hydrogenation results in reduction of the aromatic ring to yield perhydro- (or hydr-) indane (Ipatiew, Chem. Zentr. 1913, II, 1975) and finally in presence of ferric oxide on alumina (Ipatiew and Orlov, Ber. 1929, 62 [B], 593), benzenoid hydrocarbons, a resin and hydrindene are formed.

The difficulty of forming chrysene from steroid compounds by dehydrogenation over selenium or palladium was solved by Ruzicka and his co-workers who showed that temperature was the controlling factor. The same effect was noted with  $\alpha$ - and  $\beta$ -methylhydrindene which are unchanged over selenium or palladium at 360° but form naphthalene, slowly at 400°, readily at 450° (Helv. Chim. Acta, 1935, 18, 676; cf. G.P. 596191).

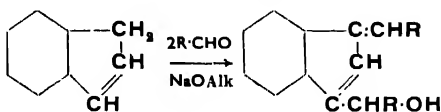
Hydrogen halides and halogens usually form simple addition products with indene. Whilst the action of hydrogen fluoride is polymerising rather than additive, chloroindane is obtained by the action of gaseous hydrogen chloride at 0° (Courtot and Dondelinger, Ann. Chim. 1925, [x], 4, 345) and less stable bromo- and iodo-analogues are obtained similarly. A liquid indene dichloride (Spilker, Ber. 1893, 26, 1541) and a crystalline dibromide (Krämer and Spilker, *ibid.* 1890, 23, 3279) have been described; both are readily converted into characteristic hydroxyhalides by hydrolysis (Brown and Howard, Ind. Eng. Chem. 1923, 15, 1147).

With nitrous acid indene affords two nitrosites (Dennstedt and Ahrens, Ber. 1895, 28, 1332). Addition of two hydroxyl groups to the olefinic bond may be effected with potassium permanganate (Heusler and Schieffer, *ibid.* 1899, 32, 29). A crystalline addition compound with nitrosyl chloride has been obtained (Perrot, Compt. rend. 1936, 203, 329).

The double linkage in the 5-membered ring of indene imparts to it many of the properties of cyclopentadiene and may also be responsible for its behaviour on oxidation, resinification and subsequent polymerisation.

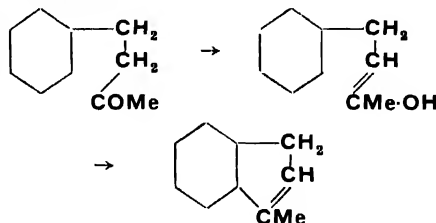
(b) Aromatic properties of indene and its derivatives call for little mention beyond that under (a). Derivatives are rarely if ever obtained by direct substitution in the aromatic ring owing to the readiness with which indene undergoes polymerisation. Derivatives of indene and especially of hydrindene of this type are purely aromatic in character.

(c) *Sodium indene* is readily formed by replacement of one hydrogen atom of the methylene group by sodium using sodamide (Weissgerber, Ber. 1909, 42, 569). The sodium can be replaced by alkyl groups yielding 1-alkylindenes (Marckwald, *ibid.* 1900, 33, 1504); these all exhibit the autooxidation behaviour of indene itself, and higher indenenes have for this reason been proposed with driers to replace linseed oil (G.P. 305515). Indene also condenses with aromatic aldehydes and ketones in presence of sodium alkoxide (Thiele and Merck, Annalen, 1918, 415, 262) to yield compounds of the type :



Somewhat similar is the reaction with ethyl oxalate in presence of alkali to yield *indene-1-oxalyl ester* (Weissgerber *et al.*, Ber. 1900, 33, 773; Thiele, *ibid.* 1900, 33, 851). With oxalyl chloride, however, a carboxyl group is introduced into the 2-position whilst *indene-1-carboxylic acid* is formed by the action of carbon dioxide on sodium indene (Wislicenus, Ber. 1911, 44, 1440; Annalen, 1924, 436, 16). As with pyrrole the methylene group of indene confers on it the ability to react with Grignard reagents with the formation of *indene-3-magnesium halides* (Courtot, Ann. Chim. 1915, [ix], 4, 76; Grignard and Courtot, Compt. rend. 1911, 152, 272).

**Indene Derivatives.**—A general method for the production of indene derivatives consists essentially in the dehydration of benzenoid compounds containing the grouping  $\text{Ar-C-C-CO}$ . Thus benzylacetone and sulphuric acid yield 1-methylindene :



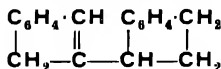
**Polyindenenes.**—The production of resinous products by the ready polymerisation of indene is of increasing industrial importance. Although the use of catalysts, *e.g.* sulphuric acid (Krämer and Spilker, Ber. 1900, 33, 2260; Weger, Z. angew. Chem. 1909, 22, 345) presents advantages, Whitby and Katz have shown that however prepared a regular series of polyindenenes is obtained which may be separated by fractional precipitation (J. Amer. Chem. Soc. 1928, 50, 1160;

Canad. J. Res. 1930, 4, 344; mechanism of polymerisation, Tammann and Pape, Z. anorg. Chem. 1931, 200, 113). A number of workers have observed that under specified conditions, e.g. using dilute sulphuric acid, molecules of relatively well-defined complexity may predominate. Thus Weger (*l.c.*) prepared a tetramer by the action of concentrated sulphuric acid on a benzene solution of indene (*cf.* Stobbe and Farber, Ber. 1924, 57 [B], 1838) whilst Krämer and Spilker (*ibid.* 1890, 23, 3278; 1900, 33, 2260) and also Marcusson (Chem.-Ztg. 1919, 43, 109, 122) obtained higher polymers  $[(C_8H_8)_n]$  where  $n=11-12$  (*paraindene*), and *metaindenes* where  $n=16-22$  are obtained by the action of sulphuric acid on indene in absence of solvent].

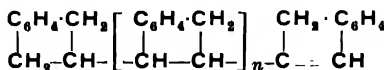
Somewhat similar control may be exercised in the use of other catalysts of which halogen hydrides (*v. supra*) and particularly Friedel-Crafts catalysts are important examples. Thus highly polymerised indenenes and resins may result from the action of oxygen and peroxides (Staudinger and Lautenschläger, Annalen, 1931, 488, 1; Adkins and Houtz, J. Amer. Chem. Soc. 1931, 53, 1058) and of stannic, antimony and boron chlorides, etc. (Staudinger *et al.*, Helv. Chim. Acta, 1929, 12, 934, 958, 962; Whitby and Katz, J. Amer. Chem. Soc. 1928, 50, 1166).

Crude polymers resulting from the action of sulphuric acid on indene are usually red, but purified products form colourless compounds the softening point of which varies quite regularly with the molecular weight. Each molecular variety contains one double bond in each molecule (for general accounts, see Risi and Gauvin, Canad. J. Res. 1935, B, 13, 228; Hugel, Bull. Assoc. franc. Techn. Pétrole, 1937, No. 39, 25).

*Di-indene*, m.p. 57–58°, contains one olefinic linkage as it readily yields a dibromide, m.p. 120°, and is oxidised by chromic acid to  $\alpha$ -hydrindone (Stobbe and Farber, Ber. 1924, 57 [B], 1838). It contains, however, only one reactive methylene group (Bergmann and Taubadel, *ibid.* 1932, 65 [B], 463) and is formulated



Whitby and Katz (J. Amer. Chem. Soc. 1928, 50, 1166) formulate higher polyindenenes similarly as they behave as unsaturated compounds



although Staudinger *et al.* represent them as large rings (Helv. Chim. Acta, 1929, 12, 934). These higher polymers undergo some depolymerisation on heating and may be hydrogenated with partial depolymerisation.

Indene polymers and coumarone resins (*v. Vol. III*, 413c) are finding application in industry, usually in association with tung oil, in paints, enamels, etc. (*cf.* U.S.P. 1019666). They are also used in other combinations as softeners for rubber (U.S.P. 2095630), adhesives (G.P. 652007), binders for tiles (Canad. P. 372911), and it has also been proposed to utilise

indene resins with formaldehyde (B.P. 319444), with pitch-resins from coal-tar (U.S.P. 1355103), and by condensation with maleic anhydride (B.P. 376479) and in other ways.

A. H. C. **INDERITE**. Hydrated magnesium borate,  $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ , occurring as small, white to pinkish, reniform nodules in red clay in the borate deposits, which were discovered in 1934 near the Inder salt lake, 150 km. north of the Caspian Sea in western Kazakhstan. The acicular, orthorhombic crystals show relations to *inoite* ( $2CaO \cdot 3B_2O_3 \cdot 13H_2O$ ). (A. M. Boldyreva and E. N. Egorova, Mat. Central Sci. Investig. Geol. Prospecting Inst. U.S.S.R. 1937, General ser. No. 2; A. M. Boldyreva, Mém. Soc. Russe Min. 1937, [ii], 66, 651; M. N. Godlevsky, *ibid.* 1937, [iii], 66, 315; G. B. Bokiy, Bull. Acad. Sci. U.R.S.S. ser. Chim. 1937, 871.) L. J. S.

**INDIAN BUFFALO GRASS** (*v. Vol. II*, 482c).

**INDIAN FIRE**, *v. BENIGAL LIGHTS*.

**INDIAN GUM** or **GHATTI GUM** is a gummy exudation from the stem of *Anogeissus latifolia* Wall., occurring in vermiform or rounded tears, coloured pale yellow and of a vitreous lustre. Soluble in water, forming a viscous adhesive mucilage.

**INDIAN HEMP RESIN** (*v. Vol. II*, 269). Indian hemp (*Cannabis indica*, *C. sativa*) is official in the Spanish, French, Belgian, Swiss and U.S. Pharmacopœias. The drug consists essentially of the resinous exudate of flowering and fruiting tops of *Cannabis sativa*, an annual indigenous to Central Asia and the Northern and Western Himalayas. Described according to origin and mode of preparation by a variety of names (e.g. *hashish*, *marihuana*, *charas*, *ganja*, *bharg*, etc.) it is one of the commonest drugs of addiction in Asia, Africa and America. Eaten or smoked it produces an intoxication commencing with a pleasant lethargy in which there is distortion of space and time followed often by horror and depression. The resin separated from the leaves and known in this form as *charas* is an important article of commerce between Turkestan and India. For reports on *C. indica* by the League of Nations Commission on Traffic in Noxious Drugs, see Amer. Chem. Abstr. 1938, 32, 8073; 1939, 33, 2283. The cultivation of *C. sativa* and its use in medicine is regulated in the U.S.A. by the Marihuana Tax Act, 1937. In the form of tincture or extract the drug has been prescribed as a narcotic and anodyne, but was removed from the British Pharmacopœia in 1932.

In North America the name Indian hemp is applied not to *C. sativa* but to *Apocynum cannabinum*, known also as Canadian hemp, which contains the cardiac glycoside cymarol (*v. Vol. II*, 8366; *Vol. III*, 538a), and accidents have been caused by the confusion of names. A comprehensive account of the hemp drugs is available in the monograph "Marihuana" by Walton (Lippincott, New York, 1938); short reviews are given by Adams (Science, 1940, 92, 115), Todd (Nature, 1940, 146, 829) and Macdonald (Nature, 1941, 147, 167).

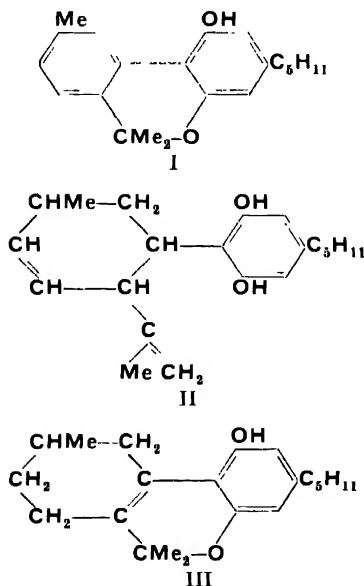
*Cannabis* resin yields on distillation an



essential oil containing *p*-cymene with small amounts of other substances including 1-methyl-4-isopropenylbenzene and  $\alpha$ -caryophyllene (Simonsen and Todd, J.C.S. 1942, 188), and a high boiling viscous liquid known as "crude cannabiol" or "red oil" which contains the active principle of the drug. From this material the following inactive compounds have been obtained:

**Cannabiol**,  $C_{21}H_{28}O_2$ , m.p. 76–77°, b.p. 140–150°/10<sup>-3</sup> mm. (bath temp.), occurs in large amounts in Indian and Egyptian resin and in smaller quantity in American resin. Its constitution as 6''-hydroxy-2:2:5'-trimethyl-4''-*n*-amyl-dibenzopyran (I) has been established by complete synthesis (Ghosh, Todd and Wilkinson, J.C.S. 1940, 1121, 1393; Adams, Baker and Wearn, J. Amer. Chem. Soc. 1940, 62, 2204). For isolation from Indian resin as *p*-nitrobenzoate, see Work, Bergel and Todd (Biochem. J. 1939, 33, 123).

**Cannabidiol**,  $C_{21}H_{30}O_2$ , m.p. 66–67°, b.p. 160–180°/10<sup>-3</sup> mm. (bath temp.), has been isolated as 3:5-dinitrobenzoate from American (Adams, Hunt and Clerk, J. Amer. Chem. Soc. 1940, 62, 196) and Egyptian (Jacob and Todd, J.C.S. 1940, 649) resin. It is considered to have structure (II) and can be cyclised to a mixture of tetrahydrocannabinols yielding cannabimol on dehydrogenation (Adams *et al.*, J. Amer. Chem. Soc. 1940, 62, 2402, 2566).



Isolation of homogeneous active substances from American resin has been reported by Haagen-Smit *et al.* (Science, 1940, 91, 602) and by Powell *et al.* (*ibid.*, 1941, 93, 522), but these claims await confirmation. The tetrahydrocannabinol (III) (6''-hydroxy-2:2:5'-trimethyl-4''-*n*-amyl-3':4':5':6'-tetrahydrodibenzopyran) obtained as an intermediate in the cannabiol synthesis of Ghosh, Todd and Wilkinson (*l.c.*) exhibits the characteristic

physiological action of hashish in animals and in man, as also do the isomeric tetrahydrocannabinols obtained by cyclising cannabidiol. A large number of analogues of these substances have been prepared and examined pharmacologically (Todd *et al.*, J.C.S. 1941, 169, 826; Adams *et al.*, J. Amer. Chem. Soc. 1941, 63, 1971, 1973, 1977). The purified cannabis resins freed from cannabiol and cannabidiol have the composition of tetrahydrocannabinol and may contain a mixture of isomers of varying activity. For fuller details of recent work the numerous publications of Adams *et al.* (in J. Amer. Chem. Soc.) and of Todd *et al.* (in J.C.S.) since 1940 should be consulted.

A. R. T.

**INDIAN OR CHINESE INK.** This is an ink in solid form, made by pounding finely divided lampblack with a solution of glue into a paste which is then moulded into sticks. An ink was prepared in China about 2600 B.C., but according to Jametel ("L'Encre de Chine, d'après des Documents Chinois," 1882) this ink was a vegetable varnish and it was not until about the third century B.C. that the product as it is known to-day was introduced. Various substances have been used as the source of the lampblack, such as rice straw, pine wood and haricot beans, but these have been replaced to a large extent by vegetable oils, especially tung oil from *Aleurites cordata*. The oil is burned in small lamps of terra-cotta, chilled by water in a small depression at the top; these lamps are placed in a terra-cotta chamber, and the smoke is collected in inverted terra-cotta cones with polished interior, from which the deposited soot is removed from time to time by means of a feather. A row of bricks supports the cones, about twenty of which are used at a time. When the ink is made on a larger scale the terra-cotta condensing vessels are replaced by a hollow wooden tunnel with a hole bored in the wall.

According to Jametel the lampblack from sesame or tung oil yields a much better quality of ink than that derived from pine wood. In Japan also either sesame or tung oil or pine wood are used for making the lampblack, and this is incorporated with strained ox-hide glue. Formerly a decoction of *Hibiscus mutabilis* Linn. was used as the medium in China, but has long been discarded in favour of glue.

At the present time the ink produced by different Chinese manufacturers differs mainly in the fineness of the lampblack and the tone of the black.

Ink is imported into this country from China in the original boxes each holding 1 lb. According to the size of the sticks, 8, 20 or 40 may go to the pound, and are spoken of in the trade as "eights," "forties," etc. The sticks are moulded in various forms, some being in squares, some in tablets and some octagonal. The best qualities of sticks are gilt and are stamped with fine impressions such as dragons, lions' heads, etc., which denote qualities well recognised in the trade, and they are also perfumed. The octagonal sticks, known as "Mandarin," are of fine quality, and are distinguished from ordinary sticks by the finer impression of the characters

on the sides. The poorest quality is in the form of small sticks and stamped with white letters.

**Examination.**—The Chinese test the quality of ink by rubbing the tablet on a porcelain palette. If the sound produced is faint the ink is considered to be of good quality (*Si-mo*), whereas a loud noise indicates an inferior quality (*Tsou-mo*). This is essentially a test for the fineness of the carbon particles. A Chinese ink of good quality should yield a uniform suspension when rubbed with water. The best inks are of a violet shade, whilst inks of the second quality are black, and inferior inks have a yellow tint.

A practical test is to stir 0.1 g. of the powdered ink in 10 ml. of water and to shake the mixture from time to time. Inks of the best quality will diffuse rapidly, whereas the cheaper grades will hardly colour the water even after several hours' contact.

The tinctorial value may be ascertained by applying successive coatings of the suspensions to equal areas of Whatman paper. The best inks can be distributed much more smoothly than those of inferior quality, and an opaque coating is attained with fewer washes.

Specimens of the four grades of ink examined by Mitchell, "Inks: Composition and Manufacture," 4th ed., 1937, p. 37, gave the following results:

Ink.	Water, %.	Carbon residuc, %.	Nitrogen in residuc, %.	Nitrogen in original ink, %.	Ash, %.
I. Octagonal stick . .	8.16	53.9	0.0	7.74	4.80
II. Lion stick, fine letters . .	7.20	52.53	—	4.87	3.69
III. Lion stick, coarse letters . .	9.93	49.64	—	7.26	4.96
IV. Small stick, coarse letters . .	9.40	57.04	—	6.84	4.01

**Liquid Indian Inks.**—A preparation for the use of artists is made by grinding up broken fragments of the Chinese stick-ink with water. Other preparations are made directly from lamp-black incorporated with a liquid medium containing a gum to keep the carbon in suspension. These are of the same type as the carbon inks which are still used in the East.

**Non-Coagulating Indian Ink.**—An ink that is claimed not to coagulate even at  $-30^{\circ}$  has been patented by Shinozaki (Japan. P. 110282, 1935). The mixture consists of glue (30 parts) previously heated for 3 hours at  $120^{\circ}$ , potassium nitrate (60 parts), urea (10 parts), urotropine (10 parts), carbon black (60 parts) and water (1,000 parts).

C. A. M.

**INDIAN MADDER** (*v.* Vol. II, 523c).

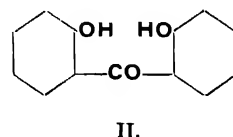
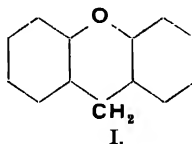
**INDIAN YELLOW, PIURI, PURREE** or **PIOURY** is a pigment used mainly in India for colouring walls, doors and lattice-work, and by artists for water-colour work. It

is, or was, made almost exclusively at Monghyr (Bengal) from the urine of cows which have been fed upon mango leaves. On heating the urine, the colouring matter separates out; this is pressed into a ball and dried partly over a charcoal fire and finally in the sun. Internally the balls are of a brilliant yellow colour, whereas the outer layers are either brown or of a dirty-green colour. The undecomposed part consists only of euxanthic acid in the form of a magnesium or calcium salt; the outer and decomposed portion contains in addition euxanthone, both free and combined. The composition of piuri appears to be variable; a fine sample, according to Graebe (Annalen, 1889, 254, 272), contained euxanthic acid, 51.0; silicic acid and alumina, 1.5; magnesium, 4.2; calcium, 3.4; water and volatile matter, 39.0%.

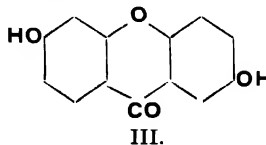
Euxanthic acid is isolated by digesting piuri with dilute hydrochloric acid and treating the residue with a solution of ammonium carbonate. Addition of hydrochloric acid to the filtered solution causes the separation of crystals of euxanthic acid. According to Spiegel (Ber. 1882, 15, 1965), euxanthic acid is decomposed by 2% sulphuric acid at  $140^{\circ}$  into euxanthone and the anhydride of glucuronic acid.

**Euxanthone, Purrenone, Purrone**,  $C_{15}H_{16}O_4$ , was first obtained by Stenhouse (Annalen, 1844, 51, 425) and shortly afterwards by Erdmann (*ibid.* 1844, 52, 365) from euxanthic acid. It forms pale yellow needles or laminæ, m.p.  $240^{\circ}$  (corr.), which sublime with little decomposition on gentle heating.

By distillation with zinc dust (Salzmann and Wichelhaus, Ber. 1877, 10, 1397; Graebe and Ebrard, *ibid.* 1882, 15, 1675), euxanthone gives methylenediphenylene oxide (I) which is converted into xanthone by oxidation, indicating that euxanthone is a dihydroxyxanthone. When fused with alkali, euxanthone yields euxanthonic acid (II), hydroquinone and resorcinol.

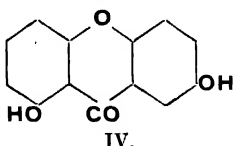


Euxanthone was first synthesised by Graebe (*l.c.*) by distilling a mixture of  $\beta$ -resorcylic acid and hydroquinone carboxylic acid; it was shown later by von Kostanecki and Newslar (Ber. 1891, 24, 3983) that the same product is obtained if in this reaction the  $\beta$ -resorcylic acid is replaced by resorcinol. Of the two constitutional formulæ (III and IV) indicated by these syn-



theses, (IV, 1:7-dihydroxyxanthone) was shown to be correct by a study of the methylation of euxanthone by means of methyl iodide (Von

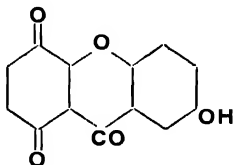
Kostanecki, *ibid.* 1894, 27, 1992). Only a monomethyl ether was obtained, indicating that euxanthone contains a hydroxyl group



adjacent to the carbonyl group (IV). Final proof of the correctness of this formula was afforded by the following synthesis of euxanthone by Ullmann and Panchaud (*Annalen*, 1906, 350, 108); condensation of 2-chloro-6-methoxybenzoic acid with the potassium derivative of hydroquinone monomethyl ether, employing copper powder as catalyst, yielded 2-(4-methoxyphenoxy)-6-methoxybenzoic acid which was converted by the action of concentrated sulphuric acid into euxanthone dimethyl ether, and this by treatment with aluminium chloride in the presence of benzene gave euxanthone.

Euxanthone forms the following derivatives: 1-methyl ether, pale straw-coloured rectangular plates, m.p. 235° (Robertson and Waters, *J.C.S.* 1929, 2239), m.p. 240° (Graebe and Aders, *Annalen*, 1901, 318, 365); 7-methyl ether, yellow plates, m.p. 130.5°; dimethyl ether, colourless needles, m.p. 149.5° (Graebe and Aders, *l.c.*); diethyl ether, prisms, m.p. 126° (Graebe and Ebrard, *l.c.*); 7-acetyl-, elongated yellow prisms, m.p. 160° (Robertson and Waters, *l.c.*); diacetyl-, pale yellow prisms, m.p. 185° (Salzmänn and Wichelhaus, *l.c.*); dibenzoyl-, colourless crystals, m.p. 221–222° (Zerner, *Monatsh.* 1910, 31, 797); 4,5-disazobenzene-, red needles, m.p. 249–250° (decomp.); acetyl-derivative, ochre-yellow needles, m.p. 197–199° (Perkin, *J.C.S.* 1898, 73, 666).

According to Nierenstein (*Ber.* 1913, 46, 649), oxidation of euxanthone with chromic acid gives the quinone:



This consists of dark-red needles soluble in alkalis with a blue coloration and converted by reduction into 1:4:7-trihydroxyxanthone.

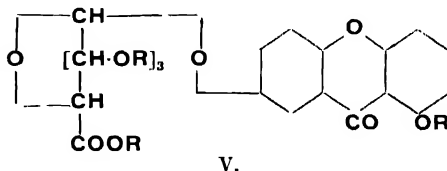
Euxanthone possesses only feeble tinctorial properties; the respective shades obtained with woollen cloth mordanted with chromium, aluminium and tin being dull brown-yellow, pale bright yellow and very pale bright yellow (Perkin and Hummel, *J.C.S.* 1896, 69, 1290).

*Euxanthic Acid* exists as a stable hydrate,  $C_{15}H_{16}O_{10} \cdot H_2O$ , melting at 150–158° with partial decomposition. The methyl ester and ethyl ester melt at 218° and 198°, respectively (Graebe *et al.*, *Ber.* 1900, 33, 3360; *Annalen*, 1901, 318, 345).

Neuberg and Neimann (*Z. physiol. Chem.* 1905,

44, 114) obtained euxanthic acid by the inter-action of a diacetyl-bromoglycuronolactone and the potassium derivative of euxanthone. The synthesis confirmed the suggestion of Fischer and Piloty (*Ber.* 1891, 24, 521) that this glycuronate is structurally analogous to a glycoside. Herzig and Stanger (*Monatsh.* 1914, 35, 47) found that the two methyl derivatives obtained by the action of diazomethane on euxanthic acid yielded, by acid hydrolysis, euxanthone 1-methyl ether, indicating that the glycuronic acid residue in euxanthic acid is attached at the 7-position.

By the action of methyl iodide and silver oxide on euxanthic acid, Robertson and Waters (*J.C.S.* 1931, 1709) obtained methyl O-tetramethyl-euxanthate (V;  $R=CH_3$ ), colourless needles, m.p. 168°. Hydrolysis of this ester with hydrochloric acid gave 1-O-methyl-euxanthone and a trimethylglycuronic acid which by oxidation with nitric acid and esterification of the product yielded the methyl ester of 2:3:4-trimethylsaccharolactone. The constitution of the latter was confirmed by synthesis from 2:3:4-trimethyl glucose. Euxanthic acid, therefore, has the following structure ( $R=H$ ):



The glycosidic linking present in euxanthic acid appears to be of the  $\beta$ -type.

The precursor of Indian yellow is mangiferin (*euxanthogen*) which is present in the bark and leaves of *Mangifera indica* Linn. (mango). Mangiferin is isomeric with euxanthic acid, to which it gives rise in the organism (Gorter, *Bull. Jard. bot. Buitenzorg.* 1922, [iii], 4, 260; see *Amer. Chem. Abstr.* 1923, 17, 1472).

A. G. P. and E. J. C.  
**INDICATORS.** In volumetric analysis indicators are substances which are used to determine end-points in titration work. The three main types of reaction, namely neutralisation, oxidation and reduction, and precipitation, which predominate in this kind of analysis, all require suitable indicators in order to determine the points at which equivalent quantities of the reacting substances have been brought together. However, the use of the numerous organic compounds which are differently coloured in acid and in alkaline solution serves not only to determine end-points in acidimetry and alkali-metry, but also to mark the end-points as within certain limits of hydrogen ion concentration. Thus indicators for neutralisation are also employed colorimetrically to determine the free hydrogen ion concentration as distinct from the total acidity in liquids: a subject of great importance in biological work. Certain types of titrations are carried out with the aid of external as distinct from internal indicators for determining the end-points. As such external indicators are really sensitive drop reagents which are specific tests for the presence or absence of

particular substances their properties will not be considered in this article.

Since the year 1913 a series of indicators depending upon a totally different principle from those adverted to above was studied by Paneth and his collaborators. The fundamental principle involved in the use of these radioactive indicators is that isotopes have identical chemical properties. If an element  $A$  has a radioactive isotope  $A'$ , the detection and determination of  $A'$  by electroscopic methods can be adapted to the detection and determination of  $A$ . A brief consideration of these indicators is given at the end of this article.

#### NEUTRALISATION INDICATORS. (*See also* CHEMICAL ANALYSIS, Vol. II, pp. 637 *et seq.*)

From the form and position of the titration curves (Vol. II, p. 639) it will be evident that for the titration of a strong acid by a strong base any indicator with a  $p_H$  range extending between the extreme limits of 3 and 11 units on this scale will give satisfactory results, if the acid and alkali are of the order of decinormal concentration. In consequence of acid hydrolysis, the titration of a weak base such as ammonia by a strong acid must be carried out with an indicator having a  $p_H$  range within the limits of about 3 and 6 units, such as Methyl Orange or Methyl Red. Similarly the occurrence of alkaline hydrolysis when a weak acid, such as acetic acid, is neutralised by a strong base necessitates the employment of an indicator such as phenolphthalein with a  $p_H$  range between 8 and 11. If the acid and alkali are of considerably lower concentration than decinormal, further restrictions within these ranges will become necessary.

The sensitiveness of indicators was first investigated by Tizard (B.A. Report, 1911, p. 208) who drew attention to a fundamental difference between two-colour indicators such as Methyl Orange and one-colour indicators such as phenolphthalein. When a two-colour indicator is used the end-point of a titration should be independent of the amount of indicator in the solution if the titration is carried to the half-way stage, because the titration is being carried to a certain *fractional* change of the indicator. With the one-colour indicators the case is different, because the titration is carried on until there is a certain *amount* of coloured substance produced or removed. Similar views, with shades of difference, were expressed by N. Bjerrum ("Die Theorie der alkalimetrischen und azidimetrischen Titrierungen," Ahrens' Sammlung, XXI, Stuttgart, 1914) who pointed out that the difference in behaviour between two-colour and one-colour indicators will hold so long as there is no great difference in intensity between the acid and alkaline colours. If, however, this difference is considerable there will be a tendency for two-colour indicators to approach one-colour indicators in behaviour. In this connection it has been pointed out by Noyes (J. Amer. Chem. Soc. 1910, 32, 815) and by Bjerrum (*op. cit.*) that the change interval for Methyl Orange is not symmetrical on account of the considerably greater intensity of the red form. It is therefore better, for experimental verification of the characteristic behaviour of

two-colour indicators, to select one of the sulphonaphthalein indicators such as Bromocresol Green, which exhibits a striking contrast between the yellow (acid) and the blue (alkaline) colour. Bromocresol Green has a  $p_H$  range from 3.6 to 5.2, and it has been found that the quantity of  $N/50$  hydrochloric acid which is required to transform this indicator in concentrations extending over a range of 1/20,000 to 1/100,000 to the half-way colour stage corresponding to a  $p_H$  value of 4.4 is strictly constant. A suitable one-colour indicator for experiments of this kind is *p*-nitrophenol, having a  $p_H$  range of 5.0–7.0 and therefore insensitive to atmospheric carbon dioxide. It has been found that the quantity of  $N/50$  hydrochloric acid required to extinguish the yellow colour of sodium *p*-nitrophenolate in solutions of concentration ranging from 1/5,000 to 1/50,000 is strictly proportional to the concentration of the indicator in the solution (Berry, unpublished work).

Reference may be made to Bjerrum's monograph for an elaborate discussion of the theory of the errors which are involved by the use of indicators in acidimetry and alkalimetry. If it is desired to titrate to a given hydrogen ion concentration it is necessary to consider two terms which have been known as the *indicator exponent* and the *titration exponent* respectively. Since the ionisation of a weak acid is regulated by the law of mass action, it follows that when an indicator is one-half ionised, the dissociation constant of the indicator is equal to the concentration of the hydrogen ions in the solution in which the indicator is one-half ionised. The indicator exponent,  $pI$ , is defined as  $-\log K$ ,  $K$  being the dissociation constant, while the titration exponent,  $pT$ , is the value of  $p_H$  corresponding to the optimum colour. At the half-way change it is clear that  $pT = pI$ . From what has been stated above it will be evident that the titration exponent of a two-colour indicator is independent of its amount in the solution, because the titration is carried to only a certain fractional change. The titration exponent of a one-colour indicator can however be varied over a short  $p_H$  range by suitable variation of the quantity of the indicator in the solution.

It has been estimated that with careful work it should be possible to titrate with a degree of accuracy corresponding to  $p_H = pT \pm 0.3$ , and by introducing colorimetric methods the error may be reduced to  $\pm 0.1$ . For a discussion on the elimination of the titration error in acidimetric and alkalimetric titrations a monograph by Brennecke may be consulted ("Newer Methods of Volumetric Chemical Analysis," edited by W. Böttger, translated by Oesper, London, Chapman and Hall, Ltd., 1938, [U.S.A. Printed], p. 3).

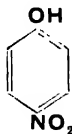
The properties of indicators have been discussed in terms of two different theories, viz. the ionisation theory largely due to Ostwald and a theory which correlates change of colour with change of chemical constitution. The idea that the colour, in organic compounds, is due to the presence of certain groupings in the molecule appears to have originated with Witt (1876). Groups such as the azo group  $-\text{N}=\text{N}-$  and the nitro group  $-\text{NO}_2$  which are considered

to be the source of colour are known as chromophores or chromogens, while groups which augment colour are known as auxochromes. Armstrong in 1888 put forward his well-known quinonoid theory of colour, a theory which with minor modifications has survived to the present time. When a colourless compound becomes coloured, e.g. when alkali is added to a compound such as *p*-nitrophenol, the benzenoid ring is considered to assume the constitution of a quinonoid nucleus. Addition of acid reverses the process. It would appear that the chief ground on which Armstrong formulated his theory was that compounds known to have quinonoid reactions are all strongly coloured.

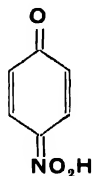
It is now recognised that neither theory alone can give an adequate explanation of the action of indicators, and that the correct way of studying the problem is by regarding indicators not as true acids or bases which ionise directly (*acid* indicators giving rise to hydrogen ions, or more correctly hydroxonium ions, and anions which are differently coloured from the undissociated molecules, and *basic* indicators giving rise to cations of different colour from that of the undissociated molecules and hydroxyl ions) but as pseudo-acids or pseudo-bases, an important conception due to Hantzsch. Pseudo-acids and pseudo-bases are compounds, electrically neutral in themselves, which can undergo isomeric changes into true acids and true bases and these latter compounds at once give rise to their appropriate ions. It must be noted that the colours of the neutral and acidic isomers of pseudo-acids must be different, and that the acidic anion must be similar in colour to that of its undissociated molecule. Similar considerations apply *mutatis mutandis* to the colours of the isomers of pseudo-bases.

Among the numerous compounds having indicator properties the following may be selected as of particular importance, both on account of their theoretical interest and their practical value, namely the nitrophenols, the phthaleins (including the sulphonephthaleins) and the azo compounds. The isomeric changes which are considered to follow the ionic changes of these classes of compounds will be briefly considered.

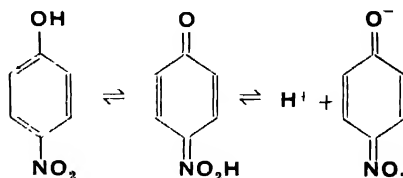
The nitrophenols, of which *p*-nitrophenol will be considered as an example, are known to give rise to two series of others, one derived from the true nitro-compound



which are colourless, the other derived from the isomeric nitronic acid form

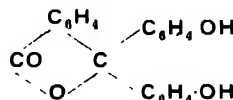


and are intensely red in colour. In the crystalline condition *p*-nitrophenol is colourless and therefore exists almost entirely as the true nitro-compound having a benzenoid nucleus. In aqueous solution, there is an appreciable yellow colour, due to the formation of a perceptible quantity of the isomeric acid form which has a quinonoid ring. This nitronic acid at once ionises into hydrogen ions and the coloured anions, the equilibrium being represented by the equation :

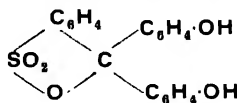


The yellow colour of *p*-nitrophenol in alkaline solution is due to the formation of water by union of the hydrogen ions derived from the nitronic acid with the hydroxyl ions from the base, resulting in the liberation of the strongly coloured anion. In acid solution these changes are reversed, and the colour is discharged in consequence of the formation of the true nitrophenol.

The phthaleins, such as phenolphthalein,

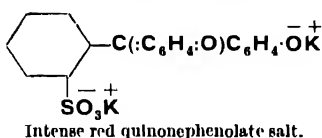
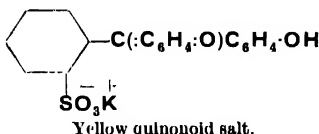
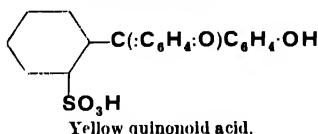
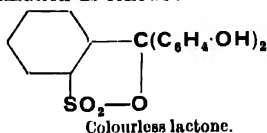


and Phenol Red, phenolsulphonephthalein,



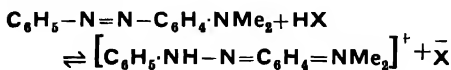
are acid indicators, the latter series having a  $p_H$  range of about 1 to 1.5 units numerically lower than the former. In a series of papers published between 1916 and 1919, Acree and his collaborators have brought forward convincing evidence that the earlier theories relating to the colour changes which phenolphthalein undergoes as being due to the opening of the lactone ring and one of the phenol groups becoming quinonoid are incomplete. White and Acree (J. Amer. Chem. Soc. 1919, 41, 1190) have concluded that the sulphonephthaleins and the phthaleins are to be considered as *dibasic* acids, the primary salt being produced from the carboxylic acid resulting from the opening of the lactone ring and the secondary salt from one of the phenol groups. Certain sulphonephthaleins such as Thymol Blue have a double  $p_H$  range, viz. from 1.2 to 2.8 and from 8.0 to 9.6, which affords additional evidence of the dibasic character of the indicator. Taking Phenol Red as a typical example of the sulphonephthalein indicators, White and Acree

represent the changes of constitution due to neutralisation as follows:



The replacement of hydrogen atoms by bromine atoms in the molecule of a sulphonaphthalein causes the colour of the alkali salts to change from red to blue. (See the Table, Vol. II, p. 640.)

Methyl Orange and Methyl Red are the most important indicators which belong to the class of azo-compounds. The parent substance, dimethylaminonazobenzene, closely resembles Methyl Orange in indicator properties. Its  $p_H$  range is 2.9-4.0, that of Methyl Orange being 3.0-4.4. The sulphonic acid group in Methyl Orange is inert, the indicator properties being determined, as in the parent substance, by the dimethylamino-group. Hantzsch and Voigt (Ber. 1929, 62 [B], 968) consider that the yellow alkaline form of dimethylaminonazobenzene has the formula  $C_6H_5-N=N-C_6H_4.N(CH_3)_2$ . When it forms a salt with an acid  $HX$  the product formed has a red cation having a quinonoid formula thus:



Although the colour of indicators in solution is determined primarily by the hydrogen ion concentration, the presence of other substances, e.g. alcohol, proteins and neutral salts, may have an appreciable influence on the colour. For a discussion of the effects of alcohol and proteins, see I. M. Kolthoff, "Indicators," translated by N. H. Furman, New York, 1926, and W. Mansfield Clark, "The Determination of Hydrogen Ions," 3rd ed., London, Baillière, Tindall and Cox, 1928. As regards neutral salts, their effect in titration work is as a rule wholly negligible (see Brennecke, *op. cit.*). When, however, indicators are used for the colorimetric determination of hydrogen ion concentration the influence of neutral salt action may assume greater importance. The general effect of

neutral salts is to cause displacement of the colour of acid indicators towards the alkaline side and of basic indicators to the acid side. It appears to be established that neutral salts cause alteration of the activity coefficients of the differently coloured forms of indicators. The influence of salts on chemical equilibria in solutions has been discussed by Brønsted (J.C.S. 1921, 119, 574) in terms of the theory of complete ionisation of strong electrolytes and activity coefficients. Kolthoff (J. Physical Chem. 1928, 32, 1820) has made a careful study of the salt error of certain indicators in the colorimetric determination of  $p_H$ , and has emphasized that indicators differ very considerably in their sensitiveness to neutral salt action. Thus Methyl Orange and Methyl Red have very small salt errors, whereas indicators of the triphenylmethane series, such as Methyl Violet and Brilliant Green, have large salt errors.

In 1888 J. J. Thomson ("Applications of Dynamics to Physics and Chemistry," London, Macmillan & Co., 1888, p. 234) pointed out that capillary forces might have marked influence on chemical equilibria. Attempts to obtain experimental verification of J. J. Thomson's ideas were not very successful until Freundlich (Liversidge Lecture, J.C.S. 1930, 164) directed attention to some experiments due to Deutsch who found that indicators in solution near their turning point changed their colours if the solution was shaken with a non-miscible liquid such as benzene. Thus if Bromthymol Blue ( $p_H$  range 6.0-7.6) is placed in a mixture of tap water and distilled water so that the blue alkaline colour is well marked; on shaking with benzene the displacement is in the acid (yellow) direction, whereas when the layers are separated the aqueous layer reverts to the blue (alkaline) colour. If a triphenylmethane dyestuff such as Brilliant Green is shaken with  $N/4$  hydrochloric acid and benzene the displacement is in the opposite (alkaline) direction. In this acid concentration Brilliant Green is yellow, corresponding to a  $p_H$  value of 0.7. On shaking with benzene the colour becomes green, corresponding to a  $p_H$  value of 2. In all experiments of this kind the changes are strictly reversible.

The indicators in the list (Vol. II, p. 640) are amply sufficient for all ordinary purposes. For particular objects other indicators may have special advantages. Mention may be made of Nitrazine Yellow (2:4-dinitrobenzeneazo-1-naphthol-3:6-disulphonic acid) which was described by Wenker (Ind. Eng. Chem. 1934, 26, 350) as a very useful indicator for work close to the region of neutrality. The colour change is from yellow at  $p_H$  6.0 to blue at 7.2, with a violet grey tint between 6.4 and 6.8. Mixtures of indicators having different absorption bands or the addition to an indicator of a dye which transforms the regular colour change into a different one more easily perceptible by the eye as in Hickman and Linstead's screened Methyl Orange (J.C.S. 1922, 121, 2502) have been recommended from time to time. Universal indicators consist of a mixture of several indicators having different colours and  $p_H$  ranges. Clark (*op. cit.* p. 97) quotes several mixtures of this kind. Other universal indi-

cators are supplied by chemical manufacturers, and they should always be used under the conditions recommended by the makers. These mixtures are useful for making rapid colorimetric  $p_H$  measurements, usually to the nearest unit, over a wide range of acidity. When the approximate  $p_H$  value has been obtained with the aid of a universal indicator, a more accurate value may be obtained by using a single indicator having a short  $p_H$  range such as one of the sulphonaphthalein series. In making determinations of this kind either a solution of known  $p_H$  value may be used for reference (see BUFFER SOLUTIONS, Vol. II, p. 120) or the colorimetry may be effected with the aid of a Lovibond comparator having standard colour discs appropriate to the individual indicators, each colour differing from the next by 0.2  $p_H$  unit. It is not difficult by estimation to obtain results accurate to 0.1  $p_H$  unit. For the colorimetric determination of titration curves without buffer mixtures a paper by Gillespie (J. Amer. Chem. Soc. 1920, 42, 742) may be consulted. See also Kilpatrick (Chem. Reviews, 1935, 16, 57).

**Fluorescent Indicators.** The determination of the acidity of dark coloured liquids, such as wines and fruit juices, may be effected by titration with the aid of indicators which show the end-point of the reaction by the appearance or disappearance of fluorescence in the liquid, the analyses being carried out in ultra-violet light. As more progress in the study of fluorescence has been made from the standpoint of physical optics than from the point of view of the constitution of substances which exhibit the phenomenon, a few notes on the subject may be added.

**Fluorescent Indicators:** An important paper on fluorescence was published by Stokes (Phil. Trans. 1852, 463) who first used the term *fluorescence* from fluor spar, as the analogous term *opalescence* is derived from the name of a mineral. Stokes considered that the wave-length of the light emitted in fluorescence is always greater than the wave-length of the exciting light. Doubt has been thrown by later work on this general principle, and in particular it has been shown by Nichols and Merritt (Carnegie Institution of Washington, 1912, Publication 152) who used spectrophotometric methods, that fluorescence can be excited in a number of substances in solution by light of greater wave-length than that at the centre of the fluorescent band. The fluorescent efficiency of dyes in solution, i.e. the ratio of the secondary fluorescent radiation emitted by the solutions to the total energy absorbed has been determined by Wawilow (Z. Physik. 1924, 22, 266). The highest value for this efficiency, viz. 0.8, was obtained for aqueous solutions of fluorescein. In methyl alcohol the value was 0.74, and in ethyl alcohol it was 0.66. The influence of solvents on the intensity of fluorescence has been repeatedly emphasised by various investigators, e.g. Fringsheim (Trans. Faraday Soc. 1939, 35, 28). In defining fluorescent efficiency as the ratio of the amount of light emitted in fluorescence to the amount absorbed, R. W. Wood ("Physical Optics," 3rd ed., 1936, p. 653) has drawn attention to an important difference

according as the measurements are made in terms of energy, or by the number of light quanta or photons absorbed or emitted.

Shortly after the discovery of fluorescein, Krüger (Ber. 1876, 9, 1572) showed that this compound could be used as an indicator in acidimetric titrations. He pointed out that it could be used in coloured solutions, and that the indicator was insensitive to carbon dioxide, which is in agreement with its  $p_H$  range as tabulated in a list compiled by Radley and Grant ("Fluorescence Analysis in Ultra-violet Light," 3rd ed., London, 1939, p. 312). Of the numerous other compounds having fluorescent indicator properties, mention may be made particularly of quinine, which has a double  $p_H$  range from 5.9 to 6.1 and from 9.5 to 10.0, of umbelliferone, first used by Robl (Ber. 1926, 59 [B], 1725), with a  $p_H$  range of 6.5–7.6, and of Acridino Orange with a  $p_H$  range of 8.4–10.4. Grant (Analyst, 1931, 56, 653) has adapted the indicator properties of quinine to the determination of the compound by titrating a known quantity in  $N/100$  sulphuric acid with  $N/100$  sodium hydroxide in ultra-violet light. A useful summary of some of the earlier work on fluorescence analysis will be found in a paper by Haidinger (Mikrochemie, 1932, 11, 429).

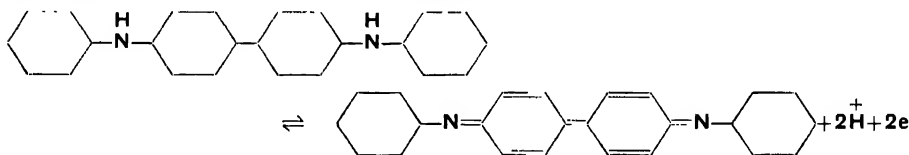
#### OXIDATION AND REDUCTION INDICATORS.

If an inert electrode, such as a platinum wire, is immersed in a solution of a substance in two different states of oxidation, such as a mixture of ferrous and ferric ions, the electrode will acquire a charge the potential of which will depend upon the experimental conditions. For any particular reversible system, the value of the potential is governed by several factors, particularly the relative proportions of the oxidised and reduced forms and the presence or absence of other ions which are capable of forming complex ions with either the oxidant or the reductant. In the absence of complications arising in consequence of the formation of complex ions, the value of the potential in any particular system is a function of the logarithm of the ratio of the concentrations, or more strictly of the activities, of the oxidised and reduced forms. Since the relation between the value of the potential and the concentrations of the oxidised and reduced ions is a logarithmic one, it will be evident that variations of these proportions will have a relatively small effect upon the potential. A considerable effect on the potential of a ferrous-ferric system may be observed by the addition of sodium fluoride, because the net effect of adding this salt is to cause withdrawal of ferric ions on account of the formation of the very stable ferriferri fluoride ions.

Conant (Chem. Reviews, 1927, 3, 1) has stressed the importance of the distinction between reversible and irreversible oxidation-reduction processes, and has pointed out that the potential has a definite meaning only when applied to strictly reversible processes. In discussing various equations for expressing potentials in terms of the logarithmic ratio of the concentrations of the ions, Conant (*op. cit.*) has pointed out the advantages of doing this on the grounds of simplicity, but added that discussion

in terms of activities is more exact, particularly for inorganic ions. As regards organic compounds, discussion of the problem in terms of concentrations is considered to be sufficiently accurate. A valuable summary of experimental work on reversible oxidation and reduction in organic systems which is of particular relevance to indicators has been published by Clark (*ibid.* 1926, 2, 127). Many organic compounds, e.g. Methylene Blue, which function as oxidation-reduction systems are strongly coloured in the oxidised condition and colourless in the reduced or leuco-condition. In the presence of a solution which has more powerful oxidising properties than the substance, the organic compound will be transformed almost completely into the coloured form, whilst with a solution having more powerful reducing properties the organic compound will change over into the colourless form. In short, Methylene Blue has the properties of an indicator. Clark (*op. cit.*) has pointed out that it should be possible to measure reduction intensities by applying colorimetric methods with oxidation-reduction indicators, just as various buffer mixtures are utilised in colorimetric investigations of  $p_H$  with the aid of acid-base indicators.

For the purposes of volumetric analysis it has been pointed out that the ideal oxidation-reduction indicator should be a substance having the properties of an oxidising or reducing agent which undergoes a striking colour change at some definite change of potential corresponding to the end-point in a reaction such as



See Kehrman and Micewicz (Ber. 1912, 45, 2641). The colour change takes place at about 0.76 volt on the hydrogen scale independently of the  $p_H$  of the solution. But the rate at which the violet colour develops when ferrous ions are titrated by dichromate increases with the acidity. The sharpness of the end-point of this titration is increased by addition of phosphate or fluoride ions to the solution so as to produce the complex ferriphosphate or ferrifluoride ions and thereby reduce the potential of the ferrous-ferric system below the value for simple ions.

*Barium diphenylaminesulphonate* is in many respects preferable to the parent substance. The colour change takes place at a potential of about 0.83 volt, and this indicator is much less subject to interference by other substances than is diphenylamine. The compound is usually employed in a solution of 0.3% concentration, two drops being sufficient for the titration of 25 ml. of a ferrous salt in  $N/10$  concentration by potassium dichromate or ceric sulphate. The colour change is from green to violet and is sharply reversible. The end-point is not strictly coincident with the equivalence point, a small correction being necessary in very exact work. The correction may however be eliminated if the

the oxidation of a ferrous salt in acid solution with potassium dichromate. The colour change should be completely reversible at the equivalence point of the reaction. It should be noted that reactions concerned with oxidation and reduction are frequently of a more complex character than those involving neutralisation. In the latter, the reactions are wholly ionic, and the corresponding colour changes of the indicator are brought about by ionic reactions accompanied by tautomeric changes. The oxidation of ferrous ions by ceric ions is similar to neutralisation as the reactions consist wholly in the transfer of electrons. Other reactions concerned with oxidation and reduction may involve irreversible changes, such as the conversion of the oxalate anion into carbon dioxide when oxalates are oxidised by permanganate in acid solution.

Few compounds fulfil the requirements of the ideal oxidation-reduction indicator. Many substances undergo remarkable colour changes when they are oxidised, but the changes are frequently of an irreversible character and on this account such compounds should be avoided for volumetric work.

*Diphenylamine* was introduced by Knop (J. Amer. Chem. Soc. 1924, 46, 263) as an indicator for the titration of ferrous salts by dichromate. The compound is first oxidised irreversibly to diphenylbenzidine, then reversibly to diphenylquinone-4:4'-dianil, with a green merquinone as intermediate, possibly according to the equation:

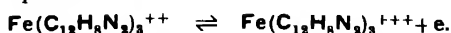
oxidising agent is standardised with the indicator under conditions as nearly identical as possible with those in which it is to be employed. Cone and Cady (*ibid.* 1927, 49, 356) have used diphenylbenzidine as indicator in the titration of zinc by potassium ferrocyanide containing a trace of ferricyanide. At the end-point the zinc is precipitated as a double ferrocyanide, so that the ratio of ferricyanide to ferrocyanide in the solution is greatly increased with the result that the indicator is oxidised to the violet colour.

Another series of oxidation-reduction indicators belonging to the triphenylmethane series of compounds was suggested by Knop (Z. anal. Chem. 1929, 77, 111). Furman and Wallace (J. Amer. Chem. Soc. 1930, 52, 2347) found two, viz. Erioglucine and Eriogreen, of value in the titration of ferrous salts by ceric sulphate.

*Tri-orthophenanthroline-ferrous sulphate*, an oxidation-reduction indicator of a different type from those previously considered, was introduced for volumetric work by Walden, Hammett and Chapman (*ibid.* 1931, 53, 3908; 1933, 55, 2649). The compound has a very stable complex cation,  $\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3^{++}$ , having a deep red colour. The change from the red ferrous complex to a pale blue ferric one takes place at a potential of 1.14



volts on the hydrogen scale according to the equation:



The indicator solution is prepared by dissolving the calculated quantity of orthophenanthroline hydrate (mol. wt. 198) in a 0.025 molar solution of ferrous sulphate containing as little free acid as possible. One drop is sufficient for the titration of 25 ml. of a *N*/10 ferrous solution with either ceric sulphate or potassium dichromate. This substance is apparently the best oxidation-reduction indicator which has so far been discovered, as the iron-phenanthroline complexes are not liable to further oxidation and foreign substances in solution are without effect upon them. Further, the addition of complex-forming ions (fluorides or phosphates) is not necessary nor is any correction required for this indicator.

For a useful monograph on oxidation-reduction indicators, see Brennecke (*op. cit.* p. 155)

#### ADSORPTION INDICATORS.

In 1923 Fajans and his collaborators introduced organic dyestuffs as indicators for the titration of silver and halide ions. Most of the early experiments were carried out with fluorescein and certain halogenated fluoresceins such as Eosin and Rose Bengal (dichlorotetraiodofluorescein) (Fajans and Wolff, *Z. anorg. Chem.* 1924, **137**, 221). Such compounds undergo striking colour changes at the end-point when solutions of halides are titrated with silver nitrate, fluorescein giving satisfactory results with chlorides, Eosin with bromides, while Rose Bengal is particularly useful for iodides. Since the colour changes with these dyestuffs take place essentially upon the colloidal dispersed particles or upon the surface of the precipitate they are known generally as adsorption indicators. Dichlor(R)-Fluorescein, having properties intermediate between those of fluorescein and Eosin, was recommended by Kolthoff, Lauer and Sunde (*J. Amer. Chem. Soc.* 1929, **51**, 3273) for the titration of chloride in very dilute solution. These indicators are generally used only in neutral solution, but Eosin may be used in very weakly acid solution. Other dyestuffs, such as Phenosafranine, first used by Fajans and Weir, and tartrazine, Berry and Durrant (*Analyst*, 1930, **55**, 613), can be used in the presence of nitric acid up to about 0.5*N*.

It has been shown that when dilute solutions of halide and silver ions are brought together, the hydrosol of the silver halide acquires a positive charge if silver ions are present in excess, whereas if halide ions are in excess the hydrosol becomes negatively charged. If an ionisable dyestuff is present in the solution, compounds can be formed either with the adsorbed silver ions and the anions of the dye, or, alternatively, between the adsorbed halide ions and the cations of the dyestuff. The colour changes which take place with adsorption indicators have been discussed by Fajans and Hassel (*Z. Elektrochem.* 1923, **29**, 495) in terms of ionic deformation phenomena on the crystal lattice of the silver halides. Kolthoff (*Chem. Reviews*, 1935, **16**, 87) is of opinion that the explanations given by Fajans are not quite accurate and has suggested

an alternative interpretation based upon exchange adsorption.

The capacity for adsorption of dyestuffs by analogous ions increases with diminishing solubility of the resulting silver halide. The solubilities of the three salts in mols. per litre are  $1.4 \times 10^{-8}$  for the chloride,  $0.725 \times 10^{-8}$  for the bromide, and  $1.0 \times 10^{-8}$  for the iodide. Dyestuffs also vary considerably as regards capacity for adsorption by a given silver halide. Thus Erythrosin is much more strongly adsorbed than Eosin, and Eosin is more strongly adsorbed than fluorescein. These differences are of great importance in the practical application of the compounds as indicators in volumetric work. Titration curves will be found in K. Fajans' monograph ("Newer Methods of Volumetric Chemical Analysis," edited by W. Böttger, 1938, p. 203). Dyestuffs of the fluorescein series and tartrazine may be used conveniently in 0.5% concentration, and one or two drops will be found suitable for the titration of halides by silver nitrate or *vice versa* in volumes of 20–50 ml. of solutions of the order of *N*/10 concentration. Phenosafranine should however be used in more dilute solution, about 0.25%. Titrations are best carried out in stoppered bottles with frequent shaking and it is desirable to add a few drops of some suitable electrolyte such as strontium nitrate solution to facilitate flocculation of the colloidal silver halide.

The properties of a few practically useful adsorption indicators for argentometric determinations are summarised in the following Table:

Indicator.	Titration with conditions	Colour change
Fluorescein.	Cl by Ag in neutral solution.	Lemon → pink. AgCl becomes pink at the end-point.
Dichlor(R)-Fluorescein.	Cl by Ag in very dilute solution.	Yellowish-green → pink.
Eosin.	— + Br by Ag in neutral or very feebly acid solution.	Yellowish - red → red-violet.
Rose Bengal.	— + I by Ag in neutral or very nearly neutral solution.	Rose in the solution to violet on the AgI precipitate.
Phenosafranine.	— + Br or Cl by Ag or <i>vice versa</i> . Best in very dilute HNO <sub>3</sub> solution.	Red ⇌ blue on the surface of the precipitate.
Tartrazine.	+ Ag in dilute HNO <sub>3</sub> solution by Cl or Br or SCN.	Dye removed from precipitate. Liquid becomes rich lemon colour.

Phenosafranine is more susceptible to interference by certain substances in solution than tartrazine. In particular, sulphates must be absent as they prevent the formation of the blue silver derivative of the compound. Rose Bengal is useful for the titration of iodide in the presence of chloride by silver nitrate (Fajans and Wolff, *l.c.*; Berry, *Analyst*, 1936, **61**, 315), as silver iodide absorbs this dyestuff strongly.

*Diphenylcarbazide* has been used by Wellings (*ibid.* 1933, **58**, 331) for determining the endpoint in the titration of cyanides by silver nitrate, the colour change from red to violet being well marked. Adsorption indicators have been used in other precipitation reactions, such as Alizarin S (sodium alizarinsulphonate) in the titration of ferrocyanides by lead nitrate in neutral solution (Burstein, *Z. anorg. Chem.* 1927, **164**, 219), and Bromphenol Blue in the titration of mercurous salts by potassium bromide and *vice versa* (Kolthoff and Larson, *J. Amer. Chem. Soc.* 1934, **56**, 1881).

#### RADIOACTIVE INDICATORS.

Electroscopic methods of detecting and measuring traces of radioactive substances far surpass spectroscopic methods of analysis in sensitiveness. Thus a quantity of  $10^{-12}$  g. of thorium-C, a radioactive isotope of bismuth, has been detected, as compared with  $3 \times 10^{-10}$  g. of sodium which has been stated to be the smallest quantity of that element detectable in the flame spectrum. In selecting a radio-element for use as an indicator it is important to avoid one which has too short a half-value period, *i.e.* the time required for the disintegration of half the initial quantity of the element. The intensity of radiation depends not upon the total number of atoms present, but upon the number of atoms which disintegrate in unit time. The practical value of radioactive indicators may now be illustrated by one or two simple examples.

Hevesy and Róna (*Z. physikal. Chem.* 1915, **89**, 294) determined the solubility of lead chromate in water as follows. To a definite amount of a soluble lead salt a known quantity of the radioactive isotope thorium-B was added. The chromate was then prepared and placed in water to obtain a saturated solution. A definite volume was then evaporated to dryness and the thorium-B on the dish determined electroscopically. The weight of lead was thus obtained and hence the solubility of lead chromate. The value obtained was  $2 \times 10^{-7}$  moles per litre at room temperature which is in good agreement with the value obtained by electrochemical methods. More recent applications of radioactive indicators to problems in analytical chemistry will be found in a paper by Rosenblum (*Chem. Reviews*, 1935, **16**, 99).

The hydride of bismuth was discovered by using thorium-C as indicator and causing hydrogen to be generated in an apparatus in which this radioactive indicator had been placed. The gas which escaped was found by Paneth to have radioactive properties (*Ber.* 1918, **51**, 1704). Having found by radioactive methods that bismuth hydride was capable of existence, Paneth and Winternitz (*ibid.* 1918, **51**, 1728)

prepared a weighable quantity of the compound from non-radioactive material.

Other examples of the use of these indicators will be found in Paneth's monograph "Radio-Elements as Indicators," McGraw-Hill Book Company Inc., New York, 1928, and in that of O. Hahn ("Applied Radiochemistry," Cornell University Press, New York, 1936).

The discovery of artificial radioactivity by I. Curie and F. Joliot (*Compt. rend.* 1934, **198**, 254) has greatly extended the possibilities of using radioactive indicators in many different types of investigations. By attacking the atoms of ordinary elements with  $\alpha$ -particles, protons, deuterons or neutrons, it is possible to prepare isotopes of these elements with unstable nuclei and consequently radioactive properties. The use of artificial radioactive elements as indicators in chemical investigations appears to have been first suggested by Grosse and Agruss (*J. Amer. Chem. Soc.* 1935, **57**, 591) who studied the exchange of bromine atoms between free bromine and sodium bromide dissolved in water. These experiments were carried out by subjecting the salt to bombardment with neutrons and thereby producing a radioactive isotope of bromine. Much progress has been made in the study of artificial radioactivity since that time, and a useful and interesting report on the subject, which includes a survey of a number of papers on radioactive indicators, has been published by Seaborg (*Chem. Reviews*, 1940, **27**, 199).

A. J. B.

**INDIGO, NATURAL AND SYNTHETIC.** Indigo is one of the most important, and at the same time the most ancient, of blue colouring matters. Extensively used for pigmenting and for dyeing both cotton and woollen materials, it was until the end of the nineteenth century obtained exclusively from a variety of plants, most of them growing in tropical countries. The discovery of the chemical constitution of the chief colouring constituent of the natural indigo, called indigotin, the invention of synthetic methods for producing indigotin from substances obtainable from coal tar, and the ultimate successful manufacture of synthetic indigo, first accomplished in Germany, constitute brilliant chapters in the history of modern scientific and industrial chemistry. The triumph of the synthetic article, however, spelt disaster for the producers of natural indigo, which, as an article of commerce, is now practically dead.

The greatest advances in our knowledge of the chemistry of the process of manufacture of indigo from indigoferous plants, and of the factors controlling the success of the operations, were gained during the last years of the nineteenth and the early years of the twentieth century by the labours of British and Dutch chemists. But these attempts to put the industry on a scientific footing came too late to save it. Far more scientific effort had been put into the search for a synthetic process, and the battle was quickly won by German dyestuff manufacturers.

Indigo is insoluble in water, and is, therefore, useless as a dye without modification. The

origin of the discovery that indigo could be dissolved in a vat of fermenting organic matter is unknown, but all early dyers must have used this process. In such a vat the indigo undergoes reduction and dissolves as "indigo-white" or leuco-indigo, which forms a yellow solution in alkaline liquors. When a piece of cloth is dipped in the liquor or "vat," it absorbs the almost colourless indigo-white, and when it is subsequently exposed to the air oxidation occurs and the blue dyestuff is formed in the cloth. The so-called fermentation vat is now only used for special purposes, mainly in the East. Chemical reducing agents are now used, the most important being sodium "hydrosulphite," ( $\text{Na}_2\text{S}_2\text{O}_4$ ), although others such as zinc dust and lime (an older process) may be used. Dyeing with indigo is dealt with more fully elsewhere (see Vol. IV, 135).

#### NATURAL INDIGO.

*Historical.*—Methods for preparing indigo from the plant are given in ancient Sanskrit records, and, although it appears to have been known to the Romans only as a pigment, there is abundant evidence that it was used in ancient Egypt for dyeing mummy cloths. Knowledge of the dyestuff is said to have been re-introduced to Europe from the East by the great traveller Marco Polo about A.D. 1300, but its use in Europe was very limited until it began to be imported early in the sixteenth century via the Cape of Good Hope. The East India Company is stated to have been exporting large quantities of indigo by 1615. Its use met with much opposition from the growers of woad, and laws prohibiting its use were enacted on the Continent and in England. It use was legally permitted in France in 1737 and gradually its merits became universally recognised. Until near the close of the nineteenth century, when the manufacture of synthetic indigotin in Germany was successfully accomplished, the cultivation of indigo-yielding plants and the extraction of the colouring matter was an important industry in tropical countries.

The most important sources of indigo for the European market were India (Bengal), Java and Guatemala, the last being of minor importance. The quality of the product varied considerably from time to time and from place to place. According to Georgievics, the best Indian indigo came from Lower Bengal and Bihar, and the quality deteriorated going from East to West. It was also grown in the Philippine Islands, China, Japan, Brazil and parts of Africa.

According to H. E. Armstrong (J. Soc. Arts, 1919, 67, 446), the acreage under indigo cultivation in India in 1897, the year in which synthetic indigo first appeared on the market, was 1,688,042; this had fallen to less than 150,000 by 1914. In 1897 India exported 169,543 cwt. of indigo worth £2,910,000, of which 62,669 cwt. came to the United Kingdom. Two-fifths of the production came from Northern Bihar, and, according to Rawson (J.S.C.I. 1899, 18, 467) the industry employed one and a half million people. The loss of this industry was a tragedy for India. A revival occurred during

the war of 1914-18 when supplies of German indigo were cut off from most parts of the world and other countries had not yet started the manufacture. The acreage under indigo rose to 316,600 in 1921-2 but thereafter diminished rapidly. At the present time there is little demand for natural indigo; in 1933 India is said to have exported but 417 cwt. of which 20 cwt. came to the United Kingdom. It is said that natural indigo is still used to some extent in the Dutch Indies for batik dyeing (J. Soc. Dyers and Col. 1937, 53, 248).

In 1916-22 a serious attempt was made, largely inspired by Professor H. E. Armstrong, to rejuvenate the natural indigo industry in India by organised research. Many people considered that by improved methods of cultivation, manufacture, organisation and salesmanship it would be possible to make natural indigo once again competitive with synthetic indigotin. An account of the whole experiment and its abandonment owing to political disturbances and financial stringency is given by W. A. Davis (Chem. and Ind. 1924, 266-268, 303-307). Some of the results obtained by Davis and his collaborators are referred to later in this article.

*The Plant and its Cultivation.*—The most important plants yielding indigo belong to the genus *Indigofera* (Fam. Leguminosae); these have been cultivated in India, China, Egypt, the Philippines, Caracas and Brazil. The following species have been cultivated for indigo manufacture: *Indigofera tinctoria* Linn., *I. sumatrana* Gaertn. (the Indian plant), *I. disperma* Linn., *I. argentea* Linn., *I. arrecta* Hochst (the Natal plant), *I. paucifolia* Delile (the Madagascar plant) and *I. serundiflora* Poir. (Guatemala plant). Less important are *I. pseudotinctoria* R.Br., *I. angustifolia* Linn., *I. arcuata* Willd., *I. caroliniana* Walt., *I. cinerea* Willd., *I. longercarnea* Boiv., *I. caerulea* Roxb., *I. endecaphylla* Jacq., *I. glabra* Linn., *I. hirsuta* Linn., *I. indica* Lam., *I. mexicana* Benth. and *I. leptostachya* D.C. In Japan, China and Russia the plant usually cultivated has been *Polygonum tinctorium* Ait. belonging to the genus *Persicaria*, and the native West African source of indigo has been almost entirely *Lonchocarpus cyanescens* Benth. The European woad plant, at one time largely grown in Europe, is *Isatis tinctoria*. Other plants which yield indigo are *Nerium tinctorium*, *Gymnema ligens* Spreng, *Eupatorium laeve* D.C., *Tephrosia tinctoria* Pers., *Marsdenia tinctoria* R.Br. and certain species of orchids such as *Phaius grandiflorus* Reirhb. and *Calanthe veratrifolia* R.Br.

The colour-yielding substance, indican, in *Indigofera* species is present almost entirely in the leaf, and to some extent in the mid-rib or rachis. According to Rawson (The Cultivation and Manufacture of Indigo in Bengal, J.S.C. 1899, 18, 467), the percentage of leaf in a well-grown plant is about 40, but other workers record values as high as 60-65%. The indigotin content of the leaf varies with the season of the year (thus Rawson found 0.2% on May 28 and 0.76% on August 25), the age of the leaf and its position on the plant. Although the maximum amount of colouring matter is present from the middle to the end of August, by this time much

leaf has been lost from the plant; manufacture is, therefore, usually started in the middle of June. Gaunt, Thomas and Bloxam (J.S.C.I. 1907, 26, 1174) record a sample of air-dried leaves of *I. sumatrana* yielding 3.53% of indigotin, against 0.6% from other samples and 1.81% from *I. arrecta*, and they suggest that cultivation and selection should increase the indigotin content of the plant.

Up to the early years of this century the plant generally cultivated in India was *I. sumatrana*, said to be a mixture of several sub-varieties. Another species, *I. arrecta* (the Natal plant), had been developed in Java by the Dutch indigo research station, and had replaced the *I. secundiflora* formerly grown. This plant was introduced into India, largely by Bernard Coventry (see Indigo Improvements Syndicate Report, 1901), and according to W. A. Davis (*l.c.*) for some years gave phenomenal results. Where *I. sumatrana* had given only 5 seers (10 lb.) of cake indigo per acre, the new plant gave yields of 20-40 seers in several successive years on many estates. Such yields enabled indigo planters to make substantial profits in competition with synthetic indigotin, but by 1915, owing to a mysterious wilt disease, the yields had fallen to only 5-7 seers per acre. Davis was successful in showing that the disease and consequent failure of the crops was due to deficiency of the soil in phosphates and organic matter caused by continuous heavy cropping without manurial treatment. It was found that *I. arrecta* could be grown with great success in Assam, especially for the production of seed which could not be produced on the impoverished soil of Bihar. For a comparison of the indigotin content of *I. sumatrana* and *I. arrecta*, see Berghoil (Report of the Indigo Research Station, Sirsiah, 1906, 1907).

According to W. A. Davis (Publications of the Agricultural Research Institute, Pusa, 1920, No. 7) high-quality plants rich in indigotin are obtained when the soil is poor in nitrogen so that the plant is forced to grow on nitrogen taken up from the air by the nodule bacteria. It seems probable that the activity of these organisms determines high indigotin content, and that the production of indican is due to the plant removing from the nodules nitrogen compounds which would be prejudicial to their continuous action. A good supply of soluble phosphates and of organic matter is necessary. Humus supplied must not contain nitrogen, and cover crops such as wheat or mustard which remove nitrogen are advantageous.

**The Manufacturing Process.**—The process of extracting indigo from the plant is a simple one, and the operations carried out in India and other places in the twentieth century are said to differ but little from those of the ancient Egyptians. There are two major operations, a steeping of the plants in water, during which a fermentation takes place, followed by an aeration of the resulting solution in a separate vessel, causing the precipitation of the indigo. The following description is given by Davis. The plant is cut in the field in the early morning, taken to the factory in bullock carts and loaded into cement-lined vats. [It

has been shown by Watson (J.S.C.I. 1918, 37, 81) that when the plant is air-dried the amount of indican present diminishes. It has long been known that the indican rapidly disappears from the freshly-cut moist leaf.] The vats are then filled with water, warmed if necessary to 90°F., the plants being kept down and held in position by cross-beams fastened across the tops of the vats. The plants are left to steep in the water about 12 hours; after about 4 hours a bacterial fermentation sets in, the effect of which is that the parent substance of the dye, the so-called *indican*, present in the leaves of the plant, passes into solution. The materials fermented consist of protein and carbohydrate exuded from the cut stems, and the gas liberated consists, in the early stages, of nitrogen and hydrogen, but in the later stages an increasing proportion of carbon dioxide is evolved and the vat liquor becomes slightly acid.

When the fermentation is complete the liquor has a slightly yellow colour and contains *indoxyl* (see p. 464c). From this liquor the dye is obtained by a process known as "beating." The liquor is run into large vats at a lower level, and is then thrown up into the air as a fine spray by means of a large paddle-wheel. The indoxyl becomes oxidised to *indigo*; after about 1½ hours the beating is stopped and the indigo is allowed to settle out as a fine blue mud. After a good fermentation the settling is nearly perfect, but with a bad fermentation it is very incomplete and 20-30% of the indigo may be lost. After settling, the supernatant liquor is carefully run off by special valves and the thick blue mud remaining is transferred to a boiling tank where water containing a small amount of dilute sulphuric acid is added and the mixture raised to the boil by live steam. This treatment prevents further fermentation and dissolves out brown impurities (*indigo-gluten*). The indigo is again allowed to settle and after the clear liquor has been run off the residue is transferred to "filtering tables," large frames across which cotton cloth is stretched, and drained. The residue is then pressed between cloths in large wooden boxes, and slabs of indigo 3 in. thick are obtained. The slabs are then cut up by wire cutters into 3 in. cubes which are dried slowly in air to a moisture content of 6%, this taking 4-6 weeks. The cubes are finally brushed, polished and packed for market in large wooden chests holding 300 lb.

**Water.**—In the manufacture of indigo, pure water in large quantities is needed. J. Bridges Lee, "Indigo Manufacture," Calcutta, 1892, recommends treating hard water with lime, and if much organic matter is present, with permanganate. Alumino-ferric may also be used (Berghoil). Davis (Indigo Publication, 1920, No. 8, Agricultural Research Institute, Pusa) says that in Assam at Panchnoi the water available for steeping gave a poor yield and quality of indigo because, coming by a small river from nearby hills, its bacterial character changed rapidly. The soft river water gave a slow growth of indican-splitting bacteria, making longer steeping necessary, and this is known to be disadvantageous.

**Extraction.**—As is to be expected, the manu-

facturing process varies in detail, in different places and at different times, and a considerable amount of experimental work on the influence of various factors is on record. The fermentation may be complete in 6 hours in very hot weather, but generally, at a temperature of 90–92°F., 12–15 hours appear to be necessary, both for *I. sumatrana* and *I. arrecta*, according to the indican content of the plant. The addition of chemicals such as mercuric chloride, sodium and potassium carbonates, lime, carbolic acid, formaldehyde and sugar does not appear to be advantageous, but sodium nitrate is said to facilitate the deposition of the indigo in the oxidising vat. The work of Thomas, Bloxam and Perkin (J.C.S. 1909, 95, 846) suggests that the addition of a small quantity of sulphuric or oxalic acid may be advantageous.

An account of a hot-water process of extraction is given by Dr. Roxburgh, dated 1797, in Bancroft's "Philosophy of Permanent Colours," London, 1813, who says that a more complete and certain extraction of the basis of indigo is effected by subjecting the plant to the action of water heated to about 150–160°F. A hot-water method of extraction was used by the Java planters using *I. arrecta*, and Rawson, who carried out experiments with the method on *I. sumatrana*, concluded that it gave a higher-quality indigo (75–77%) than did the ordinary method (50–55%), but that the method offered no practical advantage except in cold weather. For further details consult Bridges Lee (*op. cit.*), Georgievics, "Der Indigo," Leipzig, 1892, and C. Rawson (The Cultivation and Manufacture of Indigo in Bengal, J.S.C.I. 1899, 18, 467; J. Soc. Dyers and Col. 1899, 15, 166).

**Oxidation.**—Much work was also done with the object of improving the oxidation process. Rawson considered that the oxidation of the fermented liquor was improved by air-blowing, a process patented by Geneste in 1888, the yield being 20% better than by wheel beating. It had long been considered that certain "precipitants" facilitated deposition of the indigo during oxidation, their action being probably to cause a more rapid oxidation. Coventry, in 1894, patented the addition of lime in a vat intermediate between the fermentation and oxidation vats. This caused the precipitation of calcium and magnesium carbonates which carried down impurities. The supernatant liquor was run off and oxidised in the usual way, acid being added to prevent contamination of the indigo with lime. This process gave an increased yield of indigo of improved quality, not equal to the Java product, but resembling it in containing a quantity of indirubin. Caustic soda, sodium peroxide and ammonia can also be used, but the best process of all appears to be to blow ammonia, steam and air simultaneously into the vat by means of an injector. By this process Rawson claimed an increase of yield varying from 37 to 63.8% over that obtained by the ordinary oxidation process. It must be added, however, that Bergthell (Report of the Indigo Research Station, Sirsiyah, 1906) considered the ammonia process little, if any, improvement over the ordinary oxidising process when the latter is carried out under the best conditions.

Sometimes the indigo settles badly and the liquor which is run off (the "seeth" water) may contain as much as 20% of the product. Rawson recommended the addition of alkali to promote sedimentation, and Bergthell recommended aluminio-ferrie. Davis, however, as the result of later experiments (Agricultural Res. Inst., Pusa, Indigo Publication, 1918, No. 3) preferred Dhak gum which does not precipitate impurities as aluminio-ferrie does. When added 5 minutes before the heating is ended, Dhak gum in certain cases gave an increase of yield of 70% with *I. sumatrana* and 35% with the Java plant.

For the purification of the indigo paste, it appears at one time to have been the practice in the East Indies to boil it with water and soda (Bancroft), but writers such as Roxburgh and Cosigny recommended the action of dilute sulphuric acid. The practice of boiling with the diluted acid became general, and Rawson considered that the treatment improved the quality by 5–10%. After settling, the liquor was decanted and the indigo again boiled with fresh water, filtered, pressed and dried. It is said to be advantageous to dry the indigo slowly to get a strong product, because during this slow drying some impurities gradually decompose with evolution of ammonia.

As has been stated, indigo was sold in cubes, but Briggs devised an apparatus, an illustration of which appears in Bergthell's report of 1906, for drying the indigo to a powder. When synthetic indigo was marketed, the manufacturers secured an important selling advantage by offering it as a paste, of constant indigotin content, which was readily soluble in the dyeing vat. W. A. Davis, who started his work in India in 1916, quickly paid attention to this point, and he claimed to have succeeded in standardising the preparation of a similar marketable paste from natural indigo.

**Efficiency of Manufacture.**—As the above description has indicated, there are several stages in the manufacturing process where loss of indigo may occur. The chief losses are that due to incomplete extraction of the plant, believed by Rawson to be about 5%; the loss in the "seeth" water through incomplete precipitation after oxidation, which may be 10–20%, or much more in unfavourable circumstances; and the conversion of the extracted indoxyl into products other than indigotin, for Perkin and Bloxam consider that from the moment of its production by hydrolysis of the indican of the plant (*see later*) the indoxyl is undergoing destructive decomposition. Rawson in his paper on the Cultivation and Manufacture of Indigo (*ll.c.*), considered that if his suggestions were adopted there would be little room for remunerative alteration in the process, whilst Bergthell, in 1906, considered that 87% of the extractable indigotin was accounted for, and 62–72% of the theoretical yield was obtained as dry colouring matter. Bloxam (J.S.C.I. 1906, 25, 735), however, from the results of careful analysis of the daily output from the Pembrandah factory in 1904, calculated that the highest efficiency obtained did not reach 50%, the average was 25% (about 0.1495% from the

plant, which should be capable of giving 0.6%) and the lowest figure reached was 12.6%.

When natural indigo was at its zenith, very many varieties were marketed, but in later years severe competition with the synthetic article brought about a large reduction in their number. From Asia came the indigos of Bengal, Oudh, Madras, Java, Manila; from Africa those of Egypt and Senegal; and from America those of Guatemala, Caracas, Mexico, Brazil; other varieties from South Africa and the Antilles. The best varieties were those of Bengal, Java and Guatemala, that of Bengal being most widely used in England. The Java variety was of high purity and was much used for the manufacture of "Indigo Extract" (Indigosulphonic acid; see p. 450a).

A good quality of indigo had a deep violet-blue colour and acquired a coppery lustre when rubbed with the finger nail; it was light, porous and adhered to the tongue. Inferior qualities, containing much mineral and extractable matter, were dull and greyish in appearance, heavy, tough and hard, and not bronzed by rubbing. The best qualities contained 70–90% of indigotin, average qualities 40–50%, inferior qualities as low as 20%. A typical good Bengal indigo contained indigotin, 61.4%; indirubin, 7.2%; indigo brown, 4.6%; indigo-gluten, 1.5%; mineral matter 19.6%; water, 5.7%.

#### CHEMISTRY OF INDIGO EXTRACTION.

Indigo is not present as such in any indigo-yielding plant. The colour-yielding constituent of the plants cultivated for indigo is a substance which was named *indican* and was proved, after much research by many workers, to be a glucoside of indoxyl, a substance (see p. 464c) which by oxidation with air is converted into indigo. Early workers believed that the dye was present in the plant as indigo-white, the reduction product into which indigo must be converted for use as a dye (Chevreul, Ann. Chim. Phys. 1808, [1], 66, 5, 68, 284; Gerardin and Preisser, J. Pharm. Chim. 1840, [1], 26, 344), but Schunck (Phil. Mag. 1855, [iv], 10, 73; 1858, [iv], 15, 117) isolated the glucoside from *Isatis tinctoria* (woad), *Polygonum tinctorium* and *Indigofera tinctoria* (Schunck and Roemer, Ber. 1879, 12, 2311). The indican was obtained only as a syrup which could be hydrolysed in the presence of air by acids or alkalis or by an enzyme present in the plant to a sugar, then termed *indiglucon*, and indigotin. In absence of air, however, hydrolysis gave a product which did not afford indigotin on oxidation. Cold acids converted the indican into a brown powder, a complex mixture from which Schunck isolated six substances called *indihumin*, *indifuscin* and *indiretin*, all soluble in warm sodium hydroxide solution, and  $\alpha$ - and  $\beta$ -*indifulvin* and *indirubin* insoluble in alkalis. Aqueous solutions of indican decomposed on boiling, not giving indigotin but indiglucon, indiretin and indihumin, brown amorphous substances. Cold alkalis converted indican into a new glucoside, *indicanin*, hydrolysed by acids to give indiglucon and indirubin.

Lt.-Col. G. S. A. Ranking (J. Asiatic Soc. of Bengal, 1896, 65, [ii], No. 1) first suggested that

the fermented leaf extract contains a compound of indoxyl and that indoxyllic acid might also be present; and Marchlewski and Radcliffe (J.S.C.I. 1898, 17, 430) independently suggested that indican was the glucoside of indoxyl. Hazewinkel, director of the Experimental Station for Indigo, Klaten, Java, then disclosed the results of work which had been kept secret, which proved the identity of indican and stated that the sugar was dextrose (Proc. K. Akad. Wetensch. Amsterdam, 1900, 2, 512). Eventually indican was isolated in a crystalline condition by Hoogewerff and ter Meulen (*ibid.* 1900, 2, 520) from *Indigofera leptostachya* and *Polygonum tinctorium*. Perkin and Thomas (J.C.S. 1909, 95, 795) isolated the pure sugar from indican and proved that it is dextrose. Perkin and Bloxam (J.C.S. 1907, 91, 1715) also obtained the crystalline glucoside from *I. sumatrana* and *I. arrecta* as follows:—

Leaves and stems of *I. sumatrana* (1,000 g.) were treated with 4 litres of cold acetone during 7 days, with occasional shaking, and the green extract evaporated to a small bulk. Light petroleum was added, causing deposition of a brown viscous precipitate which was repeatedly agitated with small quantities of light petroleum. The product was then treated with water, giving a pale yellow liquid from which suspended matter was removed by shaking with ether. The clear aqueous solution was treated with 10 c.c. of  $N/2$  sodium carbonate and gradually evaporated *in vacuo*, giving eventually a semi-solid mass of crystals, of which 31.66 g. were obtained from 1,000 g. of leaf.

Pure crystalline indican, spear-shaped needles from water, has the formula  $C_{14}H_{17}O_6N, 3H_2O$  and melts at 57–58°. By adding boiling benzene to its alcoholic solution it is obtained anhydrous, m.p. 176–178°; this can be used as a method of purification.

A modification of the above method is described by B. A. Amin (Agric. Res. Inst., Pusa, Indigo Publication, 1918, No. 5), by which the fresh leaves are extracted with hot water, tannins, gums, etc., are precipitated by slaked lime, the solution filtered and concentrated. The indican is then extracted from the concentrate with acetone, the rest of the procedure being as in Perkin and Bloxam's method. By this method pure indican was obtained for the first time from *I. arrecta* in large quantities. Perkin and Bloxam had trouble in extracting indican from this plant, owing to the presence of kaempferitrin and a colourless sugar-like compound,  $C_6H_{12}O_6$ , m.p. 186–187°. Amin's method is quicker and more economical in solvent than that of Perkin and Bloxam.

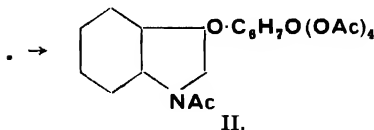
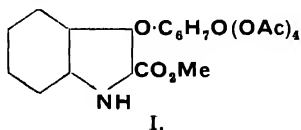
Beijerinck (Proc. K. Akad. Wetensch. Amsterdam, 1901, 3, 102) considers that the glucoside from woad, which he calls *isatan*, is not, as Schunck thought, identical with indican. Woad contains a specific enzyme, *isatase*, which does not attack indican, whilst the indigo enzyme does not hydrolyse isatan.

Indican can be detected in solution, and its amount determined, by reaction with isatin, when indirubin is formed, or by reaction with an aldehyde such as *p*-nitrobenzaldehyde, piperonal or *p*-hydroxybenzaldehyde, when the corre-

sponding indogenide is formed (Perkin and Thomas, J.C.S. 1909, 95, 795). Analytical methods are described later; for indogenides, see under INDOXYL COMPOUNDS (p. 465a).

No means appear yet to have been discovered for obtaining a quantitative conversion of indican into indigotin. There would, therefore, seem to be an inevitable loss at this stage in the manufacturing process. By hydrolysing the pure glucoside with hydrochloric acid in presence of ferric chloride as oxidising agent Hoogewerf and ter Meulen (*l.c.*) obtained 91% of the theoretical yield of indigotin; Gaunt, Thomas and Bloxam (J.S.C.I. 1907, 26, 1174) using ammonium persulphate, which had been recommended by Rawson (Report on the Manufacture and Cultivation of Indigo, Mozzufferore, 1904) obtained only 82%. Perkin and Thomas (*l.c.*) obtained a maximum of 93.5% by passing air through a solution of 0.5 g. of indican in 850 c.c. of water acidified with 15 c.c. of 33% hydrochloric acid at 60°C. Using air as oxidant, sulphuric acid gave a lower yield than hydrochloric and the filtrate was more darkly coloured. Some indirubin was always formed in these experiments. Perkin and Bloxam also studied the action of hot dilute sulphuric acid on pure indican (*cf.* Schunck's experiments, *above*) and observed the formation of substances resembling indigo brown; they also noted the formation of indole.

The synthesis of indican, identical with the material of the plant, has been accomplished by A. Robertson (J.C.S. 1927, 1937). Methyl 3-hydroxyindole-2-carboxylate was condensed with tetra-acetyl- $\alpha$ -glucosidyl bromide to give methyl 3-O-tetra-acetyl- $\beta$ -glucosidoxyindole-2-carboxylate (I). This was hydrolysed to the free carboxylic acid which, on heating with acetic anhydride and sodium acetate first at 100° then at 160° was simultaneously decarboxylated and acetylated to give 1-acetyl-3-O-tetra-acetyl- $\beta$ -glucosidoxyindole (II); this by deacetylation gave indican, which is 3- $\beta$ -glucosidoxyindole.



A. K. Macbeth and J. Pryde studied the methylation of natural indican (*ibid.* 1922, 121, 1660) and obtained a tetramethyl derivative. The sugar residue was then separated by treating with methyl alcohol containing 1% of hydrochloric acid, when a mixture of the two tetramethyl-methylglucosides was obtained, hydrolysed by acid to crystalline tetramethylglucose. Indican therefore appears to be a normal glucoside.

**The Indigo Enzyme.**—The indigo-yielding plants contain, as has already been mentioned, an enzyme capable of hydrolysing indican into indoxyl and dextrose, and this enzyme undoubtedly plays an important part in the manufacturing process. The enzyme, and its behaviour towards pure indican, have been studied by several workers. C. J. van Lookeren and P. J. van der Veen (Landw. Versuchs-Stat. 1894, 43, 401) described experiments pointing to the existence of an enzyme causing the hydrolysis of indican. Beijerinck (Proc. K. Akad. Wetensch. Amsterdam, 1900, 2, 120, 495; 1901, 3, 101) prepared it in highly active forms. He extracted finely divided leaves with cold 96% alcohol, removed the alcohol and extracted the residue with more dilute alcohol to remove chlorophyll, indican, wax, etc., and leave a highly active white powder. The enzyme is almost insoluble in water, sparingly in glycerol and more readily in 10% solutions of sodium and calcium chlorides. Ammonia destroys the enzyme. He observed that emulsin also hydrolyses indican, but only one-twentieth as fast as the indigo enzyme. Hazewinkel named the latter *indimulsin* (*ibid.* 1900, 2, 514; see also papers by Romburgh, *ibid.* 1900, 2, 344; Berghcil, J.C.S. 1904, 85, 877; ter Meulen, Rec. trav. chim. 1905, 24, 444).

The hydrolysis of pure indican by the enzyme and the oxidation of the indoxyl solution by air were studied by Thomas, Bloxam and Perkin (J.C.S. 1909, 95, 829). The fermentation was carried out in an atmosphere of pure hydrogen and the temperature and dilution, both for fermentation and subsequent oxidation, approximated to those of factory practice. Employing 2 g. of enzyme to 1 g. of indican, hydrolysis was complete in 2 hours at 50°. The solution contained only 93% of the theoretical quantity of indoxyl; 4% was adsorbed by the enzyme and the loss of the other 3% was due to "decay" of the indoxyl into products not convertible into indigotin. It was shown that by the addition of a trace of sulphuric acid to the fermentation both adsorption and decay of the indoxyl could be prevented and the yield raised to 99.5%. But although the hydrolysis could be made practically quantitative, oxidation by air at 60°C. only gave 88% of theory of indigotin, owing to secondary changes of the indoxyl. Some indirubin is formed, and products of the indigo-brown type. It was proved that a trace of ammonia (*cf.* Rawson's recommendation for factory manufacture) or lime inhibits the secondary changes of indoxyl and increases the yield of indigotin. Too much alkali, however, favours the formation of indirubin; this is probably due to production of isatin which condenses with indoxyl to form indirubin. Perkin (Proc. Chem. Soc. 1907, 23, 30) showed that Java indigos, rich in indirubin, also contain isatin. The conclusion is finally drawn that the best yields are obtained by fermenting under acid conditions and oxidising under feebly alkaline conditions. A quantitative yield of indigotin, or of this mixed with indirubin, cannot be obtained. For manufacturing purposes Thomas, Bloxam and Perkin (*l.c.*) recommended that the addition of a small quantity of sulphuric acid to the fermentation vat should be studied.

For the laboratory, however, the most satisfactory method for preparing indigotin from plant extract or from pure indican is by simultaneous hydrolysis with hydrochloric acid and oxidation.

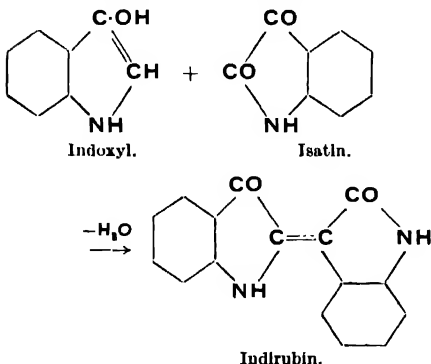
**Bacterial Fermentation.**—There is some evidence that bacteria play a minor part in the hydrolysis of indican, and in 1887 Alvarez isolated from an extract of the indigo plant an organism, *Bacillus indigogenus*, capable of producing fermentation (Compt. rend. 1887, 105, 286).

Beyerinck (*l.c.* 1900, 2, 503) studied the matter and found that infusions of garden soil had the same effect, common gas-producing bacteria being the active agents. Berthell (*l.c.*) however, found that infusions of the indigo plant invariably contained large quantities of an organism capable of producing indigo fermentation.

#### CONSTITUENTS OF NATURAL INDIGO.

Reference has already been made to the occurrence in varying amount of indirubin in natural indigo. Some further account will now be given of this and other products which accompany indigotin in the commercial product.

**Indirubin.**—Indigo was long known to contain a redder constituent of higher solubility in organic solvents, termed indigo red or indirubin. This was eventually proved to be identical with the isomer of indigotin which is obtained by condensing indoxyl with isatin thus:



At one time it was considered that two red substances might be present in indigo, but the examination of numerous samples by Perkin and Bloxam disproved this idea (*J.C.S.* 1907, 91, 279; 1910, 97, 1460). Some varieties of indigo such as that from Java and that made by the Coventry process are especially rich in indirubin, and at least a trace is probably present in all samples of the natural dye. Analyses are given by Bloxam and Perkin in the table in the next column.

It can be regarded as established that the indirubin arises during manufacture from the oxidation of some indoxyl to isatin, and the condensation of the latter with more indoxyl. This side reaction is favoured when the air-oxidation of the leaf extract is carried out under acid or alkaline conditions. Bloxam and

Indigo sample.	Total colouring matter.	Indigotin.	Indirubin.
	%	%	%
Java Indigo. New process with hot water . . .	75.20	67.67	7.43
do. . . .	73.60	63.86	9.51
do. . . .	62.91	57.35	5.01
Java Indigo. New process with cold water . . .	72.88	69.23	3.06
do. . . .	71.02	66.35	4.04
do. . . .	58.30	55.61	2.15
Java Indigo. Old process without chemicals . .	74.96	72.89	1.74
do. . . .	69.54	68.26	0.99
Coventry Process Indigo . . .	61.76	56.63	5.23

Perkin have obtained from pure indican a sample of indigotin containing as much as 25.83% of indirubin.

The presence of indirubin in natural indigo probably is responsible in part for the difference in dyeing properties between natural and synthetic indigo; it has sometimes been claimed that natural indigo gives a more attractive "bloomy" shade. Indirubin can be reduced with sodium hydrosulphite solution to a pale yellow vat which dyes wool and silk but has little affinity for cotton. Indirubin is, however, much less readily reduced than indigotin and it is said that, in practice, the indirubin settles unattacked to the bottom of the indigo vat (Matthews, *J.S.C.I.* 1902, 21, 222). Perkin has shown, moreover, that the indirubin vat undergoes further reduction to an equimolecular mixture of indoxyl and its isomer, oxindole; the indoxyl becomes oxidised to indigotin, but the oxindole is a wasted product (*Proc. Chem. Soc.* 1909, 25, 127).

Indirubin crystallises in brown needles with a metallic lustre, sublimes more readily and is less readily oxidisable than indigotin.

**Indigo Brown.**—All indigos contain an important impurity called indigo brown, which was isolated and examined by both Chevreul and Berzelius. Perkin and Bloxam examined with care the brown impurity in Bengal indigo (*J.C.S.* 1907, 91, 279). After digesting the indigo with boiling dilute hydrochloric acid to remove gluten, they extracted it with boiling pyridine. The pyridine extract contained, besides a little indirubin, three substances, (a) the main constituent,  $C_{16}H_{12}O_3N_2$  (?), insoluble in alcohol and acetic acid; (b)  $C_{16}H_{12}O_3N_2$  (?), soluble in acetic acid; and (c)  $C_{16}H_{14}O_4N_2$  (?) soluble in alcohol.

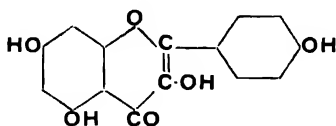
These substances are brown amorphous powders, readily reduced by zinc dust in alkaline solution giving pale brown liquids. When heated with 50% caustic potash solution they give some anthranilic acid, indicating that they are derived from indoxyl. It was stated earlier that Schunck had obtained from his indican,



among other substances, *indihumin* which he thought might be the same as indigo brown. Perkin and Bloxam by boiling pure indican with dilute sulphuric acid obtained a brown substance having a similar elementary composition to the above main constituent of indigo brown. Thus, although nothing is known of its constitution, it may be concluded that the indigo brown is derived from indoxyl during the manufacture of indigo. Analyses of indigo made by Perkin and Bloxam gave the following contents of indigo brown: Java indigo, new hot-water process, 5.4%; new cold-water process, 5.2%; ordinary process, 4.15%; Coventry process indigo, 8.7%; Bengal indigo, 9.6%; all these were from *I. arrecta*; Bengal indigo from *I. sumatrana* contained 14.0%. Indigo brown seems to have little influence on the dyeing process; its presence in large amount can be taken to indicate inefficient manufacture.

**Indigo-Gluten.**—The gluten may be obtained from indigo by extracting with dilute acid, neutralising with chalk, evaporating to dryness and extracting the gluten with alcohol. Orchardson, Wood and Bloxam (J.S.C.I. 1907, 28, 4) describe it as a horny mass, or light biscuit-coloured powder, which evolves ammonia when heated. The quantity present may be large; Perkin and Bloxam found that crude Bengal indigo (62% indigotin) lost 21.5% of its weight by acid extraction. Whether the gluten plays any part in dyeing has not been scientifically investigated.

**Indigo Yellow.**—A yellow substance in natural indigo was first reported by Bolley and Crinsoz (Jahresber. 1866, 637) who isolated from Bengal indigo, by sublimation, a yellow crystalline compound, soluble in alkali, subliming at 130°. Rawson also detected in Java indigo a similar compound having the properties of a mordant dye (J.S.C.I. 1899, 18, 251). Perkin concluded that this substance is the trihydroxy flavanol, kaempferol,



for it was shown that the leaves of *I. arrecta*, from which Java indigo is prepared, contain sometimes as much as 4% of kaempferitrin, the rhamnoside of kaempferol. This substance is not hydrolysed by the indigo enzyme, but the presence of kaempferol in the Java indigo may result from the use of sulphuric acid in the manufacturing process, the acid hydrolysing the kaempferitrin. Since the Bengal plant does not contain kaempferitrin, Perkin suggests that the indigo examined by Bolley and Crinsoz was not of Bengal origin.

**Seeth Water.**—An investigation of the product obtained by evaporating the "seeth" water, the liquor from which the indigo precipitate settles out at the conclusion of the oxidation process, was carried out by A. G. Perkin (J.C.S. 1916, 109, 210). The only definite substance isolated was a little succinic acid; the main

product was an amorphous substance resembling indigo brown, and there was also obtained a protein-like substance, about 20% of the whole, containing 8.22% of nitrogen. The "seeth" water has some value as a fertiliser.

#### THE ANALYSIS OF INDIGO.

A variety of methods have been proposed for the analysis of indigo and the literature is voluminous. The object to be achieved is generally the determination of the amount of indigotin present in the commercial indigo, a problem of no small difficulty in presence of such impurities as have been indicated above. There also come into question methods of determining the quantity of indican present in the plant, and the quantity of indigotin which the plant might be expected to yield.

Many of the methods which have been proposed for the analysis of the manufactured indigo are only of historical interest. Such are methods of extracting impurities with volatile solvents; methods of extracting indigotin with solvents such as aniline, phenol, nitrobenzene; or with acetic and sulphuric acid, although this has been used as a method of purification (Mohlau and Zimmermann, Z. Farb.-u. Textilchem. 1903, 2, 189); sublimation of the indigotin; extraction of the indigo by various reducing agents. Methods which may sometimes be of practical use are determinations by dye trials (Grossmann, J. Soc. Dyers and Col. 1897, 13, 124) and colorimetric methods. The methods of most practical importance, however, are those by which the indigo is sulphonated and the indigotinsulphonic acid is titrated with an oxidising or a reducing agent.

Oxidising agents which have been proposed for the titration are chlorine water (Berzelius), chloride of lime (Chevreul), potassium chlorate and hydrochloric acid (Bolley, Dinglers Polytech. J. 1851, 119, 114), potassium dichromate and hydrochloric acid (Schlumberger, J. pr. Chem. 1842, [i], 26, 217), dichromate and oxalic acid, potassium ferricyanide (Ullgren, Annalen, 1865, 136, 96), potassium permanganate (Mohr, Dinglers Polytech. J. 1854, 132, 363) and, in more modern times, ceric sulphate (private communication). The reducing agents which have been recommended for the titration are sodium hydrosulphite (Müller's method, cf. Bernthsen and Drews, Ber. 1880, 13, 2283) and titanous chloride (Knecht, J. Soc. Dyers and Col. 1904, 20, 97; 1905, 21, 292). Of these methods the one to which most attention has been given is the oxidation process using potassium permanganate.

**The Permanganate Method.**—To eliminate the errors due to the oxidising action of permanganate on substances other than indigotin, Rawson devised two methods. The first depended on precipitating the indigotinsulphonic acid with salt, leaving impurities in solution (*ibid.* 1885, 1, 74, 201; Knecht, Rawson and Loewenthal, "A Manual of Dyeing," 8th ed., C. Griffin, London, 1925, Vol. II, p. 815); the second depended on adding barium chloride, when the precipitated barium sulphate carried down suspended impurities. The results were identical by both methods (J.S.C.I. 1899, 18,

251). The process, using the salting out technique, is carried out as follows: finely powdered indigo, 0.5 g., is mixed with its own weight of ground glass and sulphonated in a porcelain crucible using 20 c.c. of concentrated sulphuric acid at 70° for  $\frac{1}{2}$ –1 hour; the product is diluted with water to 500 c.c. and the liquid filtered to remove insoluble impurities. 50 c.c. of this solution are mixed with 50 c.c. of water and 32 g. of common salt, and, after standing for 1 hour the precipitated sodium indigotinsulphonate is collected and freed from soluble impurities by washing with 50 c.c. of salt solution (*d* 1.2). The precipitate is dissolved in hot water, 1 c.c. of sulphuric acid added, diluted to 300 c.c. and titrated with *N*/50 potassium permanganate solution. The liquid gradually takes a greenish tint, the final disappearance of which constitutes the end of the titration. Each c.c. of *N*/50 permanganate is equivalent to 0.0015 g. of indigotin. This figure was later corrected to 0.00147.

The analysis of indigo, particularly by the permanganate method, was examined critically by Bloxam (J.C.S. 1905, 87, 974; J.S.C.I. 1906, 25, 735), Berghell and Briggs (*ibid.* 1906, 25, 729), Orchardson, Wood and Bloxam (*ibid.* 1907, 28, 4) and Gaunt, Thomas and Bloxam (*ibid.* 1907, 28, 1174).

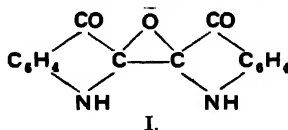
Bloxam considered that all methods of removing impurities failed when the indigotin was sulphonated only to the disulphonic acid, but found that if the sulphonation was carried to the tetrasulphonic acid, this could be precipitated in a pure form by potassium acetate. The experiments were made at first with indigo purified by sublimation from the Badische Company's synthetic "B.A.S.F. rein" material. The process is carried out thus: 1 g. of indigo mixed with 2–3 g. of powdered glass, free from iron, is sulphonated with 5 c.c. of fuming acid (25%  $\text{SO}_3$ ) for 0.5 hour, in a water oven, and the solution diluted to 500 c.c. with water; 100 c.c. of this solution are treated with 100 c.c. of potassium acetate solution (450 g. per litre), which causes precipitation. The mixture is warmed and then cooled in ice water when the tetrasulphonate separates completely in crystalline form. It is filtered on a Gooch crucible, and washed free from the brown supernatant liquor with a solution of 90 g. of potassium acetate and 5 c.c. of acetic acid in 600 c.c. of water. The product is dissolved in 200 c.c. of water, and 20 c.c. of this solution are diluted with 80 c.c. of water, and after addition of 0.5 c.c. of sulphuric acid, titrated with permanganate (1/1000). The factor given is 1 c.c. of 1/1000 permanganate = 0.00222 g. of indigotin; Rawson's figure of 1 c.c. *N*/50 = 0.00147 when calculated to 1/1000 permanganate is rather higher, namely 0.00237. It was shown that pure indigo when mixed with indigo brown and indigo-gluten gave accurate results by this method. Further, Perkin and Bloxam (J.C.S. 1910, 97, 1473) have analysed natural indigo by this method, determining the indigotintetrasulphonic acid after isolation and re-solution, by titration both with permanganate and titanous chloride, and they obtained results by both methods identical within the limits of experimental error with

those obtained by a method involving an initial extraction of indirubin by pyridine (*see below*).

**Reduction Methods.**—The reduction methods of determining indigotin depend on the fact that both hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) and titanous chloride reduce indigotinsulphonic acids quantitatively to the leuco-compounds. Both of these reducing agents are unstable on exposure to air, and special precautions have to be taken to protect the standard solutions from oxidation. Titanous chloride is the less unstable of the two, moreover the technique of its use is now so well known that it is to be preferred. Knecht (*l.c.* 21, 292) found that when the reduction of the indigotinsulphonic acid by titanous chloride took place in presence of mineral acid the end point was indefinite, but sharp results were obtained when the titration was carried out in presence of a tartrate, namely Rochelle salt. Bloxam, however, preferred to use sodium tartrate as it is more soluble than Rochelle salt. The method used by Knecht is to sulphonate 1 g. of indigo with 5 c.c. of 100% sulphuric acid at 90° for 1 hour, dilute to 300 c.c., treat with 12 g. of chalk, cool and make up to 500 c.c.; 50 c.c. of this solution are mixed with 25 c.c. of 20% solution of Rochelle salt and titrated whilst boiling with titanous chloride. Bloxam sulphonates 1 g. of indigo with 20 c.c. of 100%  $\text{H}_2\text{SO}_4$ ; the product is diluted to 500 c.c. and 25 c.c. of this, requiring 4 g. of sodium tartrate, are titrated with titanous chloride solution containing 1 c.c. of conc. hydrochloric acid in 50 c.c.

Jones and Spaans (J. Ind. Eng. Chem. 1916, 8, 1001) have suggested titrating sulphonated indigotin with sodium formaldehydesulphoxylate.

Unlike the above reduction processes, the oxidation of indigotinsulphonic acid by permanganate is not quantitative in the sense of consuming stoicheiometrically related quantities of the reagent. Standard empirical conditions must be observed to obtain quantitative results for analysis. Whereas complete oxidation to isatinsulphonic acid would require 0.4824 g. of potassium permanganate per gram of indigotin, actually only 0.45 g. is needed to decolorise the indigotinsulphonic acid. Perkin and Bloxam (J.C.S. 1910, 97, 1462) consider that two explanations are possible, either that the oxidation to the isatin stage proceeds in two steps, an intermediate compound, possibly the sulphonic acid of (I) being formed; or that two products are formed by two separate reactions, one



being possibly a dehydroindigotinsulphonic acid. These, however, are speculations. Later work by Heinisch (Färber-Ztg. 1918, 29, 183, 194) showed that when sulphonated indigotin was titrated with permanganate at the very high dilution of 1 part of indigotin in 20,000 of water, the permanganate used corresponded with 9 atoms of oxygen to 5 mol. of ind

instead of the 2:1 ratio required for isatin formation.

#### ANALYSES OF INDIGOS RICH IN INDIRUBIN.

Indirubin and its sulphonic acid are less readily attacked by both oxidising and reducing agents than indigotin and its sulphonic acid; consequently when the mixed sulphonic acids are being titrated with permanganate, titanous chloride or hydrosulphite, the indigotinsulphonic acid is to some extent preferentially attacked. It has been claimed by Rawson that an approximate estimate of the indirubin present may be obtained from the colour change towards the end of the permanganate titration; and Knecht makes the same claim for the titanous chloride process. Other workers, including Bloxam and Perkin, and Koppeschaar (*Z. anal. Chem.* 1899, **38**, 1) do not agree. Generally, for indigos rich in indirubin, it is preferable to extract the latter with a solvent before sulphonating.

For the extraction of indirubin, ether was used by Rawson, glacial acetic acid by Koppeschaar and acetone by Gardner and Denton (*J. Soc. Dyers and Col.* 1901, **17**, 170). Bloxam and Perkin re-examined the question and concluded that the solvent power observed of ether and acetone for indirubin was in reality due to their alcohol content. Acetic acid was fairly satisfactory, but pyridine was better and they devised a method based on its use (for details, see *J.C.S.* 1910, **97**, 1460). The indirubin extracted by the pyridine contained some indigotin. It was sulphonated, after it had been freed from indigo brown, and the indirubin and indigotin contents were determined by comparison in a Duboscq colorimeter with mixtures of standard solutions of sulphonic acids of pure indirubin and indigotin. The residual indigotin, after extraction with pyridine, was freed from indigo-gluten and determined, for example, by the tetrasulphonate method.

**Determination of Indican in the Leaves of Indigo Plants.**—Considerable research was devoted to devising a means for estimating the indican content of plants, this being among the data necessary for determining the efficiency of the manufacturing process. Rawson devised a process consisting in extracting the leaves (20 g.) for 2 minutes with boiling water (250 c.c.) and simultaneously hydrolysing the extracted indican with hydrochloric acid and oxidising to indigotin with ammonium persulphate. This process was later improved to give a higher yield of indigotin by Berthel and Briggs (*J.S.C.I.* 1906, **25**, 734) and by Orchardson, Wood and Bloxam (*ibid.* 1907, **26**, 4).

A better method was later devised, based on the reaction of indoxyl with isatin to give indirubin. Orchardson, Wood and Bloxam (*loc. cit.*) proceed as follows: to 250 c.c. of plant extract, from 5 g. of leaf, is added 0.1 g. of isatin and the mixture is boiled in a flask for 5 minutes, to expel air, whilst carbon dioxide is passed through. By means of a tap funnel 20 c.c. of hydrochloric acid are added and the liquid is kept boiling for 30 minutes. The precipitated indirubin is filtered, washed with hot 1% sodium hydroxide and then with acetic acid, dried and

weighed. The indirubin obtained is practically pure (98.5%) and the weight can be taken for calculating the indican content of the sample; or for greater accuracy it can be sulphonated and titrated with titanous chloride. This method gives quantitative figures with pure indican, and higher figures both with pure indican (15%) and with leaf extract (25%) than the persulphate process, probably because persulphate has an oxidising action on indigotin.

#### ANALYSIS OF SYNTHETIC INDIGO.

Synthetic indigo can, of course, be determined by sulphonation and titration with permanganate as described for natural indigo, and with the synthetic product the difficulties due to the presence of so many impurities do not arise. W. Thomson (*J. Soc. Dyers and Col.* 1921, **37**, 166) gives directions for the use of the permanganate method for the analysis of 20% indigo paste. Ceric sulphate has found application in an industrial laboratory for the determination of indigo, after sulphonating. As with permanganate, the method is empirical, and comparative titrations are carried out on a sample of pure standard indigo and the sample to be tested. The sample of indigo to be analysed is first extracted with hot hydrochloric acid (2.5 g. of indigo, 100 c.c. of water and 30 c.c. concentrated acid at water-bath temperature) for 10 minutes, filtered, washed and the loss in weight determined. About 1 g. of the dried, extracted indigo is sulphonated in a test tube with 12.0 c.c. of concentrated sulphuric acid (*d* 1.84) for 1 hour at 75°, and the mixture poured into 500 c.c. of water. After adding washings, the whole is made up to 1 litre, filtered, and 50.0 c.c. of the solution, diluted with 300 c.c. of water are titrated, in a 7 in. porcelain basin, the ceric sulphate being run in at the rate of about 6.0 c.c. per minute until the greenish colour disappears. The end point is observed best by running in 3 or 4 drops of ceric sulphate solution and stirring slowly, a streaky effect showing that indigotin is still present.

The ceric sulphate solution used for the titration is prepared by dissolving by warming 20 g. of technical ceric sulphate in a mixture of 41 c.c. of concentrated sulphuric acid and 400 c.c. of distilled water. The solution is cooled to room temperature, filtered through glass wool and made up to 1 litre with distilled water. The strength should be adjusted so that 50 c.c. of sulphonated indigo solution (about 0.05 g. of indigotin) is equivalent to 45 c.c. of the ceric sulphate solution.

An electrometric method for determining indigotin, especially in reduced indigo preparations, has been described by Strafford and Stubbings (*J.S.C.I.* 1938, **57**, 242). It consists in adding a known amount of hydrosulphite to reduce the indigo present, and following the electrical potential whilst titrating with Fehling's solution. The potential curve gives the amount of hydrosulphite and of leucoindigotin present, and from the former the amount of indigotin reduced by the added hydrosulphite can be calculated. For details the original must be consulted.

A colorimetric method for determining the

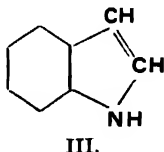
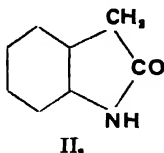
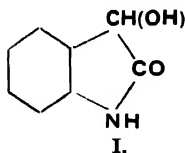
indigo content of a vat is described by J. Lotichius (J. Soc. Dyers and Col. 1939, 55, 87; 1940, 56, 433). A known amount of the vat is oxidised by hydrogen peroxide in presence of sodium protoalbinat which prevents precipitation of the indigo so that a blue sol is obtained. This, after suitable dilution, is compared colorimetrically with a sol of known indigo content or with a dyestuff solution of similar shade, such as Sirius Blue B, which has been standardised against a known indigo sol.

### SYNTHETIC INDIGOTIN.

Pure indigotin is a solid substance which can be crystallised from a number of solvents, especially from phthalic anhydride, from which it separates in beautiful blue prisms, which when rubbed have a coppery sheen. It is insoluble in water, acids and alkalis and cold alcohol; slightly soluble in hot alcohol and acetone, more readily in chloroform and glacial acetic acid, readily in boiling aniline, nitrobenzene and phenol. It can be volatilised giving a violet vapour, its density corresponding with the formula  $C_{16}H_{10}N_2O_2$ . Its absorption spectrum shows a maximum at  $\lambda 5900\text{Å}$ . in xylene, and  $\lambda 6015\text{Å}$ . in tetralin.

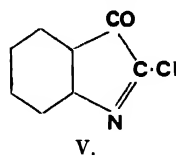
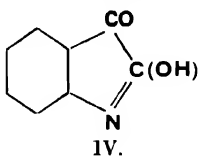
**Chemical Structure and Early Synthetic Methods.**—The chemical structure of indigotin was elucidated by the German chemist Adolf von Baeyer, after he had devoted many years to the study of the dyestuff and compounds related to it. He devised, in the course of his work, several methods by which indigotin could be prepared artificially, but it was not his fortune to discover a process which was suitable for manufacture; this problem was solved by others.

Baeyer has himself disclosed the motives which inspired his work on indigo in a paper which tells the story of his researches down to 1880 (Ber. 1900, 33, Sonderheft, LI). In 1826 Unverdorben had obtained aniline by dry distillation of indigo, and later, in 1841, Fritzsche had obtained anthranilic acid, which was later to be of such importance for indigo manufacture. Thus the benzenoid character of indigotin was fully established, and in 1841 Erdmann, and independently Laurent (1842), had obtained isatin by oxidation of indigo. Baeyer decided to investigate isatin, especially the problem of reducing it back to indigotin. This work led to the discovery of dioxindole (I), oxindole (II) and eventually of indole (III), which was

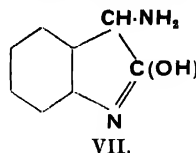
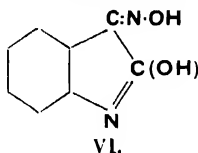


obtained by Baeyer and Emmerling by fusing *o*-nitrocinnamic acid with potash and iron filings (*ibid.* 1869, 2, 680).

The following year the same chemists obtained some indigo by heating isatin with phosphorus trichloride and acetyl chloride in presence of a little phosphorus at  $75-80^\circ$  (*ibid.* 1870, 3, 514). Baeyer returned to the consideration of this reaction 8 years later. By then he had concluded that isatin had the formula (IV), and



he realised that, to convert isatin into indigo, he must attack the carbon atom which is attached to the nitrogen atom. He, therefore, now used phosphorus pentachloride and obtained an intermediate substance, to which he assigned formula (V). This was readily reduced by a variety of agents, including ammonium sulphide, to indigotin. For about 8 years after 1870 Baeyer left the indigo field to Kekulé, who was trying to synthesise isatin without success. About 1878 Baeyer took up the subject again. He succeeded in nitrating phenylacetic acid to the *o*-nitro-derivative, and on reduction this readily gave oxindole by ring-closure. To make the indigotin synthesis complete it was now necessary to convert oxindole into isatin. This was done through nitroso-oxindole (VI) and amino-oxindole (VII), the latter giving isatin

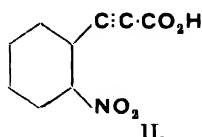
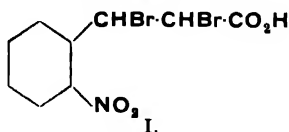


on oxidation (*ibid.* 1878, 11, 584, 1228). An independent synthesis of isatin from *o*-nitrobenzoyl chloride through *o*-nitrobenzoyl cyanide and *o*-nitrobenzoylformic acid was accomplished by Claisen and Shadwell (*ibid.* 1879, 12, 350). When the nitro-group of this acid is reduced the resulting *o*-aminobenzoylformic acid undergoes ring-closure, thus confirming the suggestion made by Kekulé (*ibid.* 1869, 2, 748) that isatin is the inner anhydride or lactam of this acid.

So far no synthesis of indigotin having any technical importance had been discovered, but when Baeyer turned his attention to *o*-nitrocinnamic acid the outlook changed; from this time (1880) onwards, all discoveries having the slightest chance of being workable were patented, and the Badische Anilin- und Soda-Fabrik took an active interest in the search for an indigo synthesis.

A vast amount of time and trouble was expended in trying to devise a satisfactory synthesis from *o*-nitro-substituted acids, ketones, etc., of the benzene series. The methods all broke down, however, on account of low yield

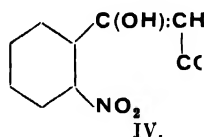
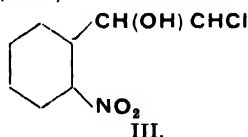
or of difficulty in getting the requisite *o*-nitro-compound. Generally *o*-nitrobenzaldehyde was needed as a starting material, a substance notoriously difficult to get. Baeyer's first success was obtained by converting *o*-nitrocinnamic acid through its dibromide (I) into *o*-nitropropionic acid (II), which with mild reducing agents gave indigotin (*ibid.* 1880, 13, 2254):



Indigotin.

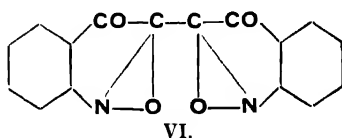
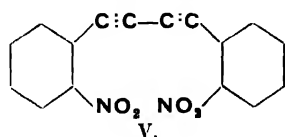
This process was patented (G.P. 11857), and was sold to the Badische Co. and the Höchst Farbwerke jointly.

Another method devised was that involving addition of hypochlorous acid to *o*-nitrocinnamic acid to give (III), followed by removal of HCl to form *o*-nitrophenyl- $\beta$ -hydroxyacrylic acid (IV), which on heating gave indigotin (Ber. 1880, 13, 2262):



Indigotin.

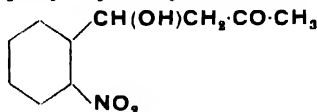
Another synthesis of great theoretical interest was from *o*-nitrophenylacetylene, obtained by heating *o*-nitrophenylpropionic acid in water. The copper compound of the acetylene when mildly oxidised with ferricyanide gave dinitro-diphenyldiacetylene (V), converted by fuming



sulphuric acid into an isomeric compound, di-isatogen (VI) which by reduction gives

indigotin (*ibid.* 1882, 15, 50). Baeyer's synthesis of indoxyl (which *see*) and thence of indigotin by oxidation follows similar lines.

*o*-Nitrobenzaldehyde was condensed by Baeyer and Drewsen with acetone to form  $\beta$ -hydroxy- $\beta$ -*o*-nitrophenylethyl methyl ketone,



which is converted into indigotin by simple treatment with alkali (*ibid.* 1882, 15, 2856); instead of acetone, other substances such as pyruvic acid could be used.

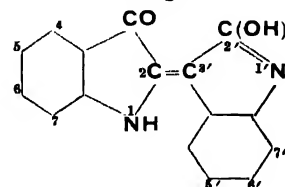
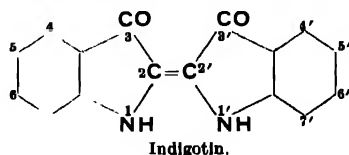
Of all the above processes, only two achieved transitory practical application. *o*-Nitrophenylpropionic acid was sold, as its sodium salt, by the Badische Co., to be made up into a printing mixture immediately before use with a thickener, a xanthate as a reducing agent and borax as a mild alkali. Its use was restricted owing to its high cost and the objectionable odour of the xanthate. Kalle and Co. marketed the bisulphite compound of Baeyer and Drewsen's ketone as "*Indigo Salt*," also for calico printing, but it had a restricted use.

**Structure of Indigo.**—As a result of his work, extending over about 18 years, Baeyer in a masterly paper (*ibid.* 1883, 16, 2188) formulated his views on the structure of isatin, indoxyl, the indogenides and finally of indigotin. The formulae which he advanced have stood the test of time and have been the foundation on which a vast chapter of chemistry has been built up (*see* INDIGOID DYE STUFFS). The matter is referred to again, however, under structure and colour (*see* p. 447a).

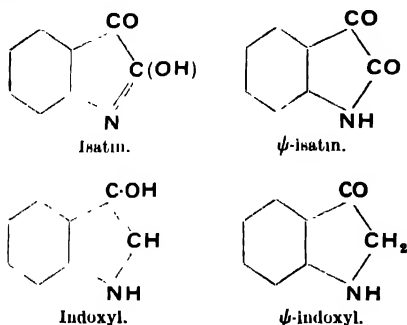
The arguments leading to this formula for indigotin were briefly:

- (1) Indigotin contains two imino groups.
- (2) The carbon atom next to the benzene ring must carry an oxygen atom.
- (3) The formation of indigotin from dinitro-diphenyldiacetylene proves the presence of the chain  $C_6H_4 \cdot C \cdot C \cdot C \cdot C \cdot C_6H_4$ .

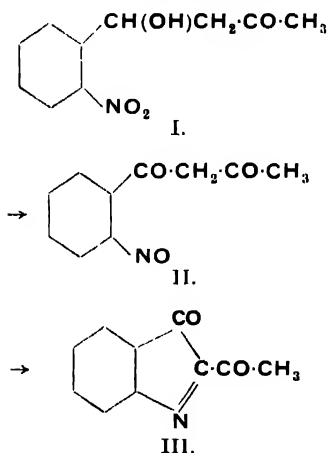
Indigotin must be closely related to indirubin; the two are isomeric, and since indirubin must be the  $\beta$ -indogenide of isatin, indigotin must be the  $\alpha$ -indogenide. The formulae with conventional numbering are given below:



Baeyer pointed out clearly in this paper that both isatin and indoxyl are capable of reacting in two forms, owing to the lability of a hydrogen atom. He gave to the compounds and their *pseudo-forms* the following formulae:



An explanation of the formation of indigotin from Baeyer and Drewson's *o*-nitrobenzaldehyde-acetone condensation product has been advanced by T. Tanasescu and A. Georgescu (Bull. Soc. chim. 1932, [iv], 51, 234). They suppose that the ketol (I) passes with loss of water into the *o*-nitroso-compound (II) which, in

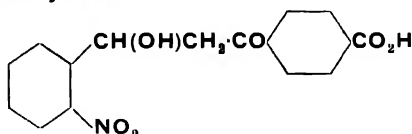


presence of alkali cyclises to (III), 2 mol. of which by hydrolysis give acetic acid and 1 mol. of indigotin.

The first claim to have synthesised indigo was made by Emmerling and Engler (Ber. 1870, 3, 885), who obtained a very small quantity by heating *o*-nitroacetophenone with zinc and soda-lime. Much doubt was thrown upon their claim as for a long time the experiment could not be repeated successfully, but it was eventually admitted that a trace of indigo can be thus obtained. Later it was shown that *o*-aminoacetophenone, and especially *o*-amino-*ω*-chloro-(bromo-)acetophenone can thus be converted into indigo. It has recently been shown by P. Ruggli and H. Reichwein (Helv. Chim. Acta, 1937, 20, 913) that while the free amine gives a very low yield of indigotin a much improved

yield, as high as 73%, can be obtained by acetylating the amino group and heating the *o*-acetamino-*ω*-bromoacetophenone with alkali in an air current.

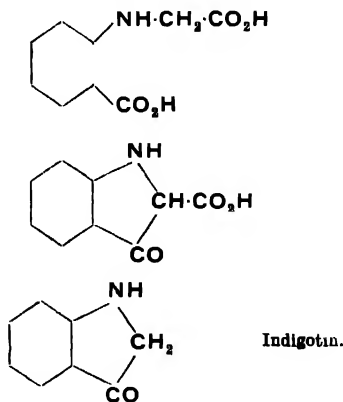
The ketols obtained by condensing *o*-nitrobenzaldehyde with acetophenone and its substitution products also give indigotin with alkali. I. Tanasescu and A. Baciū (Bull. Soc. chim. 1937, [v], 4, 1673) have shown that negative substituents in the benzene ring of the acetophenone favour indigotin formation, and in particular the compound from acetophenone-4-carboxylic acid,



passes quantitatively into indigotin by simple dissolution in alkali.

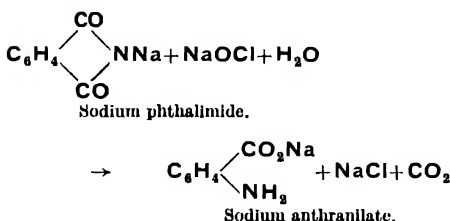
#### MANUFACTURE OF SYNTHETIC INDIGO.

The discoveries underlying modern manufacturing methods for indigo were made by K. Heumann, of the Zurich Polytechnic (Ber. 1890, 23, 343), who in 1890 observed that both phenylglycine and phenylglycine-*o*-carboxylic acid are transformed into indoxyl by fusion with caustic potash. The processes were patented (G.P. 54626, 56273, and numerous additions) and were acquired by the Badische Anilin- und Soda-Fabrik. The yield from phenylglycine was very small; that from the phenylglycine-*o*-carboxylic acid was better, and it was on this process that attention was concentrated. As has been shown by published experimental results, yields of indigo as high as 89% of theory can be obtained by fusing phenylglycine-*o*-carboxylic acid with 12-16 mol. proportions of caustic potash at 260° for 10 minutes and oxidising the indoxyl formed (M. Phillips, J. Ind. Eng. Chem. 1921, 13, 759). Caustic soda gives lower yields than caustic potash. The reactions involved are the following:



This process was the one utilised by the Badische Co. in the first successful manufacture of synthetic indigotin, which was launched on to the

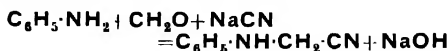
market in 1897. There were many difficulties, however, to be overcome before the project became a success, and the Badische Co. alone is said to have expended £1,000,000 in research and experiment before manufacture succeeded. Phenylglycine-*o*-carboxylic acid, which was to be the starting-point of the synthesis, had to be manufactured from anthranilic acid and chloroacetic acid. In view of the enormous quantities of anthranilic acid that would be required, its preparation from *o*-nitrotoluene was not feasible. Fortunately, another process was available, namely, the application of the well-known Hofmann reaction to phthalimide. Sodium phthalimide is treated at a low temperature with sodium hypochlorite when the following reaction occurs:



The phthalimide for this process is readily obtained by the action of ammonia on phthalic acid or anhydride. Fortunately at about this time there was discovered a cheap and facile process for obtaining phthalic anhydride by the oxidation of naphthalene with sulphuric acid in presence of mercuric sulphate. Thus it was possible to found the synthetic indigo industry at once on a cheap, abundant raw material, naphthalene. At the same time the success of the enterprise must turn on the economical utilisation of all materials and the recovery of by-products. The manufacture of phthalic anhydride used up vast quantities of sulphuric acid which were converted into sulphur dioxide. This large production of sulphur dioxide was re-oxidised to sulphuric acid by the "contact" process, a process for the manufacture of sulphuric acid which undoubtedly was stimulated by the development of indigo manufacture. The ultimate success of the first synthetic indigo manufacture is attributed to the courage, inventive genius and perseverance of Rudolf Kniesch of the Badische Co.

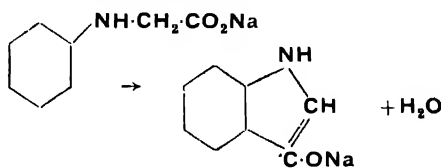
The next important discovery bearing on indigo manufacture came from a source outside the dyestuff firms. The Deutsche Gold- und Silber-Scheideanstalt in Frankfurt a/M. were manufacturers of sodamide, for sodium cyanide, and one of their chemists, J. Pfefer, discovered that the conversion of phenylglycine into indoxyl in the alkali melt goes much more smoothly, in fact practically quantitatively, when sodamide is used instead of sodium hydroxide. This discovery immediately put the manufacture of indigo in a new light, since aniline now became a competitor of anthranilic acid as starting material. It is true that the Pfefer process was also applicable to phenylglycine-*o*-carboxylic acid, but any improvement due to such a modification could hardly off-set the lower price of aniline compared with anthranilic acid. The

process was acquired by the firm of Meister, Lucius and Brünig, who at about the same time discovered an important new method of manufacturing phenylglycine without using chloroacetic acid. They applied some earlier work of Bender and of Miller and Plüchl on anhydroformaldehyde-aniline, and showed that phenylglycine-nitrile could be readily and quantitatively obtained from aniline, formaldehyde and sodium cyanide (G.P. 151538, 1901):



Subsequent hydrolysis of the nitrile gives the glycine.

These two discoveries paved the way for what is now, probably, the only practically worked process for indigo manufacture; in brief, the preparation of phenylglycine from aniline, formaldehyde and sodium cyanide; fusion of the sodium phenylglycinate with mixed caustic potash and soda in presence of sodamide; and oxidation of the indoxyl by means of air. Water is formed during the cyclisation and it is the function of the sodamide in the fusion to counteract the destructive effect of this water at the high temperature used:

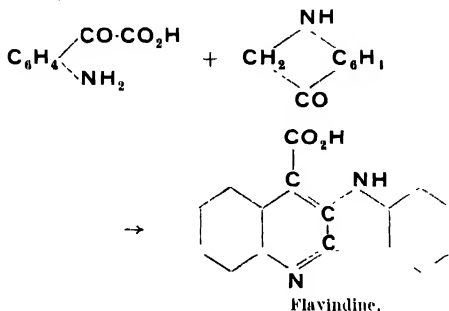


and 1 mol. proportion of sodamide should suffice for this purpose.

Details of the above fusion and oxidation processes are given by Fierz-David, "Künstliche organische Farbstoffe," Berlin, 1920, pp. 441-443, and by F. Henesey (J. Soc. Dyers and Col. 1938, 54, 105). The two descriptions differ in detail, from which one can infer that the processes employed differ in different factories. It can be gathered from the descriptions that the phenylglycine may be used as a mixture of sodium and potassium salts; that the mixed alkali used is about 4 times the weight of the phenylglycine, and may contain KOH:NaOH in the ratio 2:1. The sodamide may, according to Fierz-David, be made *in situ* in the fusion pot by passing dry ammonia into the vessel containing a mixture of caustic soda and potash at 350°; and adding sodium whilst the mass is allowed to cool. The glycine salt is added at a temperature of about 180°. According to Henesey the fusion is finished at 220° in an inert atmosphere, and is complete in 5½ hours; Fierz-David gives a fusion temperature of 190-210° and a total duration of 2½ hours. Henesey claims that the best yield is obtained using 2 mol. of sodamide per mol. of phenylglycine. At the end of the fusion the mass is discharged into ice and water, thus keeping the temperature below 50°, and is air-blown to oxidise the indoxyl to indigotin. According to Henesey the concentration of indoxyl at this stage should be about 4% and of alkali about 6% (these figures should represent

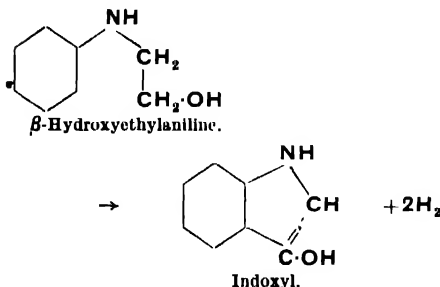
the proportions of glycine to alkali used in the fusion, which Henesey does not give) and the temperature should not exceed 70°. The precipitated indigotin is filtered in a press, washed with water, then washed in a vat with dilute acid to remove alkali, finally filter-pressed and washed again. It is then ready for standardising.

An important part of the process is the recovery of the alkali by concentration of the dilute solution obtained after the filtration of the indigotin. The yield of indigotin is given by Henesey as about 62.5% on the phenylglycine. There are, however, recoveries which bring the yield much higher. During the fusion, some 8% of the glycine is hydrolysed to methyl-aniline and aniline, which are recovered; and during the oxidation some anthranilic acid is formed, which is also recovered. Another by-product formed in small amount is *flavindine* (quindoline-4-carboxylic acid), formed by interaction of isatin (or the corresponding acid) and indoxyl, thus:



Fierz-David claims that the over-all yield of indigotin by the process is about 90% of theory.

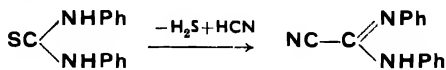
Only brief reference can be made to two other processes which have been used for the manufacture of indigo. The Badische Co. is said to have manufactured large quantities of indigo between 1912 and 1914 by alkaline fusion of  $\beta$ -hydroxyethylaniline, obtained from aniline and ethylene chlorohydrin (*see* Fierz-David, *op. cit.* 443-44). The fusion follows much the same course as that of phenylglycine, except that a mixture of caustic alkali and quicklime is used:



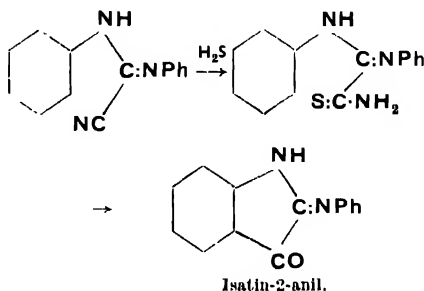
and the formation of indoxyl is accompanied by that of hydrogen.

Another synthesis is that of T. Sandmeyer (*Z. Farb.-u. Textil-chem.*, 1903, 2, 129), which, although it failed to be applied for the

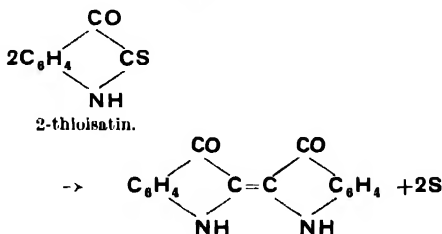
synthesis of indigotin itself, yet served as the cheapest process for isatin and its substitution products. Unlike the other technical syntheses it arrives at indigotin through an isatin derivative. The synthesis starts with thiocarbanilide, obtained quantitatively from aniline and carbon disulphide. This is treated simultaneously with lead oxide and hydrocyanic acid, when it is converted quantitatively into "hydrocyano-carbodiphenylimide" (cyanodiphenylformamidine):



The last compound when treated with yellow ammonium sulphide is transformed by addition of  $H_2S$  into a thioamide which is converted by concentrated sulphuric acid into isatin-2-anil, m.p. 126°,



The anil is readily hydrolysed by boiling dilute acid to isatin and aniline. It can be converted into indigotin by reduction with ammonium sulphide in alcoholic solution; or it can be converted by means of sodium hydrosulphide into  $\alpha$ -thioisatin which, when treated in aqueous suspension with sodium carbonate decomposes into indigotin and sulphur:



(For a full description, *see* H. E. Fierz-David and L. Blangey, "Grundlegende Operationen der Farbenchemie," 4th ed., 1938.) Sandmeyer's process, which gives an over-all yield of 80% of theory, was used for manufacture for a time by J. R. Geigy & Co. of Switzerland. One of its drawbacks was its extensive use of sulphuretted hydrogen, a dangerous industrial poison.

In 1914 the manufacture of synthetic indigo was confined to two firms in Germany, the Badische Co. and Meister, Lucius und Brünig; and one in Switzerland, the Society of Chemical



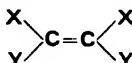
Industry in Basle. The firm of Meister, Lucius und Brünig had started to build a factory, and nearly completed it, at Ellesmere Port in Cheshire, when war broke out in 1914. This factory was opened for indigo manufacture by Messrs. Levinstein Limited, and eventually became absorbed into the British Dyestuffs Corporation and then into Imperial Chemical Industries Limited.

After the war of 1914-18 manufacture was successfully taken up in the United States, France, Italy and Japan. Russia was reported to have started a factory in the Ukraine in 1936, but by 1939 this attempt was said to have been unsuccessful. It may be that the saturation point has been reached. Already in 1926 Fierz-David estimated the output at 10,000,000 kg., about 10,000 tons, of 100% indigotin per annum. It seems probable, too, that for some of its uses indigo has been, and is being, displaced by newly discovered dyestuffs.

#### THE STRUCTURE AND COLOUR OF INDIGO.

Although Baeyer's formula for indigotin is in a general way satisfactory, and no responsible chemist doubts that the component atoms of the molecule are combined as the formula shows, many chemists have felt that it does not satisfactorily account for the behaviour and properties of the substance. There are three principal facts which the formula, as ordinarily written, does not account for:

- (1) As an ethylenic compound of the form

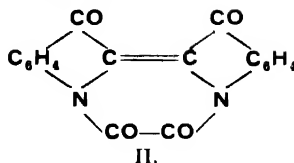
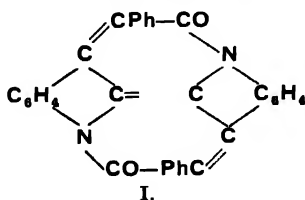


indigo should exist in two isomeric forms, *cis* and *trans*; only one form is known.

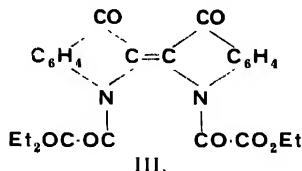
- (2) The two keto- and two imino-groups are comparatively indifferent towards the usual reagents which attack such groups.
- (3) On existing theories of colour the intense colour of indigotin is scarcely to be expected from the structure ascribed to the compound.

It seems probable that all these facts are to be ascribed to a common cause, and that a satisfactory formula should account for them all. It must be remembered that a satisfactory theory must not only account for the colour of indigotin but also for that of thioindigo and all the other types of indigoid dyes.

The question whether indigotin itself has the *trans* or *cis* structure may not be answerable from chemical evidence. When indigotin is condensed with 2 mol. proportions of phenyl-acetyl chloride, the derivative (I) is formed which must be derived from *trans* indigotin.

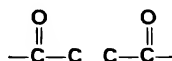


This substance has a red colour and, according to Posner (Ber. 1926, 59 [B], 1799) its absorption spectrum is of the same type as that of indigotin, as is that of the corresponding derivative from indigotin and ethyl malonate. On the other hand the oxalyl derivative (II), which can be obtained from indigotin and oxalyl chloride in pyridine at room temperature (Van Alphen, *ibid.* 1939, 72 [B], 525), must be a *cis*-indigotin derivative. This compound is yellow, but its *dianil* is red-violet and the diethoxyoxalylindigo (III) is also red-violet (Van Alphen, Rec. trav.

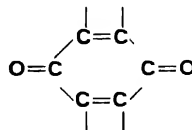


chim. 1939, 58, 378). The crystal form of indigotin is said to indicate a *trans* structure (A. Reis and W. Schneider, Z. Krist. 1928, 68, 547).

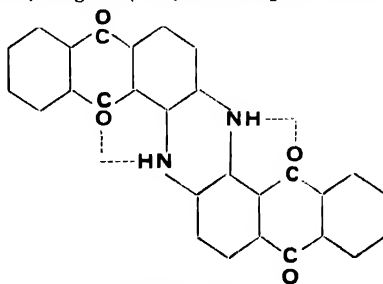
The chromophore of indigotin may be regarded as the grouping



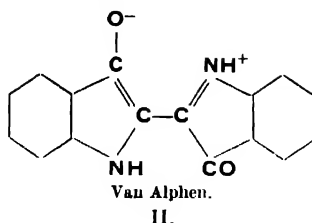
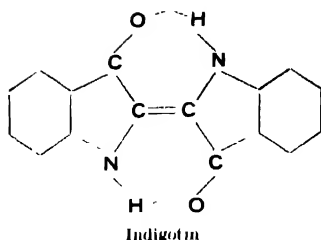
which is the grouping characteristic of all indigoid compounds. The auxochrome is to be regarded as the NH or C<sub>6</sub>H<sub>4</sub>-NH group. It is to be noted that the chromophore is the same as that present (in a double form), in benzoquinone



Since the group NH is a stronger auxochrome than S, indigotin (blue) has a deeper colour than

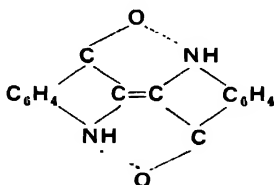


Indanthrene blue.



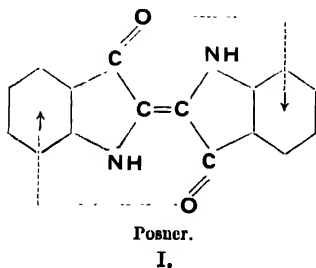
thioindigo (red). R. Robinson (J. Soc. Dyers and Col. 1921, **37**, 77) pointed out that the blue colours of indigotin and of Indanthrene Blue are probably due to the same cause, the interplay of partial valency forces between the CO and NH groups. Forces of this kind would stabilise indigotin in a *trans* form and no *cis* form could exist. A similar idea was put forward by Scholl and Madelung independently (see Madelung and Wilhelmi, Ber. 1924, **57** [B], 234).

In recent times the theory has been advanced that hydrogen can act as a co-ordinating element; it might play such a rôle in indigotin, and this would account for the suppression of keto- and imino-properties; but such co-ordination can have little to do with the colour of indigotin, for the N-alkyl and other derivatives of indigotin which have no imino-hydrogen are also deeply coloured, as are also thioindigos, etc. Madelung (*l.c.*) favours a formula in which partial valency is active between the O of the keto group and the N of the imino group thus:



At the same time he shows that the oxygen of the keto-group may be displaced by the :NH, :NPh and :NOH groups (by indirect methods), the resulting compounds all being spectroscopically similar to indigotin.

Posner (*l.c.*) discussed the different formulae which had been proposed, and suggested a new one, in which the residual valency of the keto-group interacts with the far benzene ring as indicated in (I). Van Alphen, on the other hand,

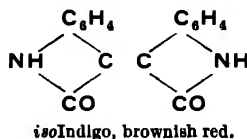
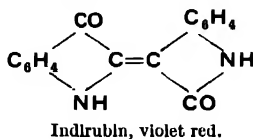


considers that the properties of indigotin can only be accounted for by the simultaneous existence of a number of "resonance hybrids" of which (II) may be one (Rec. trav. chim. 1938, **57**, 911).

The following Table (Posner) shows the effect of substitution in the NH group on the position and intensity of the principal absorption band of indigotin. It is to be noted that all substitution lowers the intensity very considerably, even when the effect is bathochromic. Thioindigo, however, has the same intensity as indigotin.

Substance.	mμ max.	Relative intensity.
Indigotin . . . . .	591	1.00
NN'-diethylindigotin . . . . .	652	0.31
NN'-dibenzoylindigotin . . . . .	575	0.31
NN'-diacetylindigotin . . . . .	545	0.35
7:7'-dimethylindigotin . . . . .	604	0.54
N - benzoyl - 7:7' - dimethylindigotin . . . . .	575	0.31
Indigotin phenylacetic ester . . . . .	555	0.31
Indigotin malonic ester . . . . .	550	0.31
Thioindigo . . . . .	540	1.00

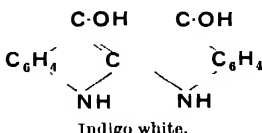
The writer is of opinion that, in the consideration which has been given to the colour of indigo dyes, insufficient attention has been paid to the indirubin and *iso*indigo series. In indigotin the auxochromic effect of the NH group is at a maximum; indirubin is much redder than indigotin, and *iso*indigo has lost all blueness.



The effect on the colour of indigotin of substitution in the benzene ring is comparatively simple. Substitution generally has a bathochromic effect, i.e. moving the absorption bands towards longer wave-lengths, except in positions 6 and 6' (for numbering, see p. 443d) where the effect is

hypsochromic. These remarks apply particularly when the substituent is methyl-, chloro-, bromo- or alkoxy- (see Formánek, Z. angew. Chem. 1928, 41, 1133). Although indigos containing many other substituents in different positions have been described, no exact comparisons of their absorption spectra have been published.

**Leucoindigo; Indigo White.**—Amongst the numerous reduction products of indigotin which are known, only one is of technical importance, indigo white or leucoindigo. This reduction product is formed by the addition of two hydrogen atoms to the two ketonic oxygen atoms of indigotin, the process being analogous to the reduction of a quinone to the corresponding hydroquinone:



Indigo white and the corresponding reduction products of other indigoid dyes have the valuable properties that they form alkali salts which are soluble in water; that in this form they have affinity for textile fibres; and that they are readily re-oxidised, generally by air, into the dyes from which they have been derived. Indigoid dyes are all applied to textiles in the form of their leuco-compounds. In practice the most important reducing agent for dyeing is sodium hydrosulphite,  $\text{Na}_2\text{S}_2\text{O}_4$ . For printing purposes, especially for discharge printing, sodium or zinc sulfoxylate, stabilised by combination with formaldehyde, is generally used. Before the introduction of these substances, glucose in presence of alkali had been much used in printing with indigo. In the fermentation vat, which is now little used in Europe for dyeing but still persists in the East, indigo is reduced to indigo white by products of the fermentation of carbohydrates by bacteria and yeasts. A very smooth reduction of indigotin to indigo white is effected by hydrogen in presence of nickel suspended in aqueous alkali. This process is said to have been employed technically for the manufacture of indigo white. Another reaction of technical interest by which leucoindigo may be produced is that between indoxyl and indigotin in presence of alkali, whereby both are converted into the leuco-compound:



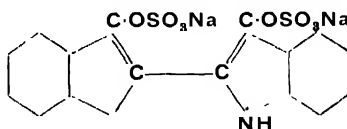
By this reaction it is possible to convert the indoxyl melt from phenylglycine directly into leucoindigo (Imperial Chemical Industries, B.P. 417862).

Indigo white can be obtained crystalline by acidifying a hot solution obtained by reducing indigo with zinc and aqueous caustic soda and cooling. Leucoindigo is marketed both as a concentrated solution containing soda or  $\text{NH}_3$  and in the solid form. It is more stable when isolated by acid precipitation than in presence of alkali. Numerous processes have been

patented for improving pastes and other preparations of leucoindigo by addition of such substances as calcium chloride, molasses and other forms of sugar, glycerol, etc., and many devices for preparing stable dry powders have been protected by patents. Leucoindigo behaves as a dibasic acid and its acid salts are much more soluble than the neutral salts, a fact which can be utilised in the preparation of concentrated solutions. The magnesium salt is sparingly soluble.

Leucoindigo can be both acylated with acid chlorides and alkylated or benzylated with appropriate reagents. The last property is utilised technically in the process of discharge printing. A quaternary ammonium compound, obtained by combining, for instance, dimethylaniline with benzyl chloride and sulphonating (marketed as "Leucotrope W") is used to assist the removal of reduced indigo, by forming a water-soluble benzyl derivative; in this way a white discharge can be obtained in printing.

**Indigosol.**—A very important step forward in the technique of dyeing with indigotin was made in 1922, when M. Bader and C. Sunder of the Swiss firm of Durand and Huguennin invented a product now marketed as "Indigosol O or DH." Indigosol, which has the structure shown, is the sodium salt of the disulphuric



ester of leucoindigo. The sulphuric ester is formed by the action of chlorosulphonic acid or sulphur trioxide on leucoindigo in pyridine or other tertiary base such as dimethylaniline (B.P. 186057). The advantage of indigosol is that it has the properties of an acid dyestuff and can be dyed on to wool from an acid bath; when dyeing wool from an indigo vat great care must be taken not to damage the wool by the action of alkali. It is said that dyeings of better fastness to rubbing are obtained with indigosol than by vat dyeing, owing to better penetration of the soluble dye in the fabric. The colour is developed on the cloth dyed with indigosol by treatment with an oxidising agent such as sodium nitrite or bichromate and dilute sulphuric acid. Indigosol also finds important application in calico printing. Processes for dyeing and printing with Indigosol are described in a series of patents (B.P. 202630; 202632; 203681; 218649; 220964; see also M. Bader, Chim. et Ind. 1924, Special No., 449; F. Peterhauser, J. Soc. Dyers and Col. 1926, 42, 152; 1927, 43, 251). Besides indigotin itself, many other indigoid dyestuffs are marketed as indigosols. A careful study of indigosols has been published recently by P. Ruggli and M. Stäubli (Helv. Chim. Acta, 1940, 23, 689).

An alternative process for preparing the sulphuric esters of leuco-derivatives of vat dyes was discovered independently by Morton, Sundour Fabrics, later Scottish Dyes Limited, who treated the dyestuff itself with sulphur trioxide

and a metal such as copper in the presence of pyridine (B.P. 245587; 248802; 251491; 258626). This process is particularly suitable for vat dyes of the anthraquinone series (*v.* ANTHRAQUINONE DYESTUFFS, Vol. I, 429a).

Other methods of obtaining soluble derivatives of indigo have since been proposed, particularly for use in printing. The Society of Chemical Industry in Basle have condensed leuco-indigo with chloroacetic and  $\beta$ -chloropropionic acids; the products are for use in printing, being oxidised by such agents as ferric chloride (B.P. 291768/1927). The I.G. Farbenindustrie patented the condensation of leuco-indigo (B.P. 330579) or of indigo itself (B.P. 324119/1928) with *m*-chlorosulphonylbenzoic acid. The products were claimed for use in printing (B.P. 337846). Unlike the indigosols, the indigo condensation product is hydrolysed by alkalis to the dye.

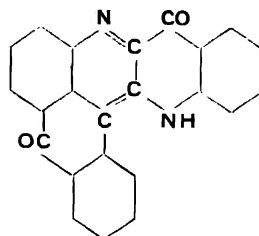
**Indigo Derivatives as Dyestuffs.**—Many indigo derivatives, substituted indigos which are still vat dyestuffs, are dealt with in the article INDIGOID DYESTUFFS. There are, however, a few other derivatives of indigotin of different character, which may be mentioned here.

**Indigo Carmine, Indigo Extract.**—It was discovered as early as 1740, by Barth, that indigo could be converted by sulphuric acid into a water-soluble dyestuff. The product so obtained was known as "*Indigo Extract*" and was used as an acid dye for wool.

A similar product is manufactured from synthetic indigo by converting it into the disulphonic acid. As a dyestuff it has poor light-fastness and its use has declined. As a foodstuff colour its use is permitted in the U.S.A. and in Australia. The disulphonic acid of commerce (disodium salt) is the 5:5'-derivative (Vorländer and Schubart, Ber. 1901, **34**, 1860); further sulphonation gives the 5:5':7-tri- and 5:5':7:7'-tetra-sulphonic acids (E. Grandmougin, Compt. rend. 1921, **173**, 586).

**Indigo Yellow 3G Ciba.**—In 1910 it was discovered that when indigo is treated with benzoyl chloride under certain conditions (*see below*) a valuable yellow vat-dyestuff was formed (B.P. 29368/1910) which appeared on the market as "*Indigo Yellow 3G Ciba*." This discovery was made by Engi and Fröhlich, Engi being a chemist of the Society of Chemical Industry in Basle who was responsible for many important discoveries in the indigoid field. Engi provisionally regarded the new dyestuff as a simple derivative of indigo having the formula (I) (Z. angew. Chem. 1914, **27**, 145), but doubt was thrown on this conception and in 1926 T. Posner and R. Hofmeister (Ber. 1926, **59** [B], 1827), on

account of the intense colour of its vat and its stability to oxidising agents, considered that it had lost its indigoid character and become converted into an anthraquinone derivative (II).



Posner's formula.

II.

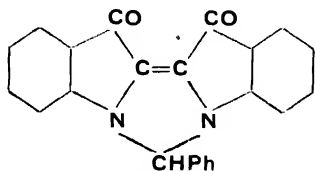
Later the question was re-investigated by E. Hope and collaborators in England (J.C.S. 1932, 2783; 1933, 1000) and by H. de Diesbach and collaborators in Switzerland (Helv. Chim. Acta, 1933, **16**, 148; 1934, **17**, 113; 1936, **19**, 1213; 1937, **20**, 132; 1940, **23**, 469). The problem involves four complex compounds obtained by the action of benzoyl chloride on indigotin.

(1) The first is the so-called Dessoulayvy compound, obtained by acting on indigotin with excess of boiling benzoyl chloride until the blue colour disappears, and adding alcohol or benzene; it forms colourless crystals, m.p. 238°. It is also obtained from NN'-dibenzoylindigotin and benzoyl chloride and contains chlorine.

(2) The so-called *Hochst Yellow R*, which can be obtained by simple hydrolysis of the Dessoulayvy compound, Cl being replaced by OH. It is isomeric with dibenzoylindigotin and is sometimes obtained as a by-product in the preparation of Indigo Yellow 3G.

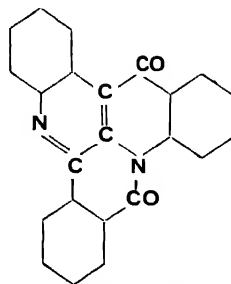
(3) *Indigo Yellow 3G*, obtained by heating indigotin with excess of benzoyl chloride in nitrobenzene in presence of copper powder at 150–160°. H. de Diesbach showed that the nitrobenzene acts as an oxidising agent and that oxygen or air increases the yield.

(4) *Hochst Yellow U*, which is formed when *Hochst Yellow R* is heated with concentrated sulphuric acid on the water bath. Both Hope and de Diesbach rejected Posner's formula for Indigo Yellow 3G and put forward alternative proposals. de Diesbach's formulæ for two of these compounds are given below:

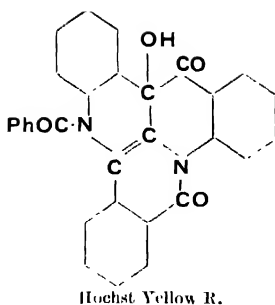


Engi's formula.

I.



Indigo Yellow 3G.



Indigo (or Ciba) Yellow 3G is brominated to give a dibromo-derivative, "*Ciba Yellow G*," said by Engi to be a still faster vat-dye. The latter was reduced in alcoholic alkali by such reducing agents as hydrosulphite to give a redder vat-dye of uncertain constitution, "*Ciba Yellow 5R*."

When indigotin is condensed with 2 mol. proportions of phenylacetyl chloride it gives a brilliant red compound, "*Ciba Lake Red B*," discovered by Engi in 1911, which is used for the manufacture of pigments of high fastness to light.

**Commercial Forms of Synthetic Indigo.**—Synthetic indigo is marketed in Great Britain by Imperial Chemical Industries in the following forms which correspond closely to those of Continental manufacturers; "*Indigo LL powder*" and "*Indigo LL 20% paste*"; "*Indigo Grains 60%*," a solid form of the leuco-compound; "*Indigo LL Vat I*," a ready-prepared leuco-solution for wool dyeing; and "*Indigo LL Vat II*," a leuco-solution for cotton dyeing.

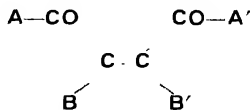
**Literature.**—Besides the references given in the text above, information is obtainable from the following sources: History of the Indigo Synthesis, A. von Bayer, Ber. 1900, **33**, Sonderheft, LI; H. E. Fierz-David, "Künstliche Organische Farbstoffe," Berlin, 1926, pp. 428 *et seq.*; J. Martinet, "Matières Colorantes; L'Indigo et ses Dérivés," Paris, 1926; Beilstein, Handbuch der organischen Chemie, 4th ed., 1936, **24**, 417.

E. H. R.

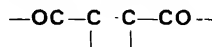
**INDIGOID DYESTUFFS.** The indigoid dyestuffs comprise a large class of colouring matters which are closely related to indigotin in their chemical constitution and are dyed by similar methods, involving reduction to a soluble leuco-compound, application to the material to be dyed and subsequent re-oxidation thereon to the colouring matter. These dyestuffs have been discovered and developed almost entirely since 1900. Several factors contributed to their rapid development after this date. The first was the chemical knowledge gained during the intensive study of indigo itself which culminated in its successful manufacture by the Badische Co. in 1897. When the problem of indigo was solved, the knowledge acquired was turned to the production and study of numbers of its derivatives and congeners. A second factor was the improvement and simplification of the old, uncertain and difficult indigo vat-dyeing process through the researches of the dyestuff manufacturers, particularly the introduction of stable

forms of the reducing agent, sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ). The way was thus prepared for introducing new vat-dyes to the dyers. A third factor was the discovery by Friedländer in 1905 of thioindigo, a red dyestuff, which, with its derivatives, immediately extended the range of shades obtainable with vat dyes. During the decade following this discovery there was intense activity in developing this field of dyestuffs, many new dyes being marketed by Kalle and Co. of Biebrich, who first manufactured "*Thioindigo Red*" in 1906; by Meister, Lucius and Brummig of Höchst; and by the Society of Chemical Industry of Basle. The manufacture of these dyestuffs is generally more difficult than that of indigo itself and they are not produced on so large a scale as indigo. Nevertheless their properties, their brilliance of shade and all-round fastness are so attractive that they can sell at a price which is about five or six times that of indigo. Although first introduced for dyeing wool, which they leave in a much softer condition after dyeing than do those dyes needing a chroming treatment to render them fast, they are now largely used also in calico printing, and provide a range of shades including brilliant oranges, scarlets and blues, besides browns and greys.

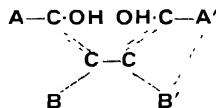
A satisfactory definition of indigoid dyes is not easily given in a few words. In the broadest sense, the class includes all dyes of the general formula



where the bonded pairs A and B and A' and B' respectively link the chromophore



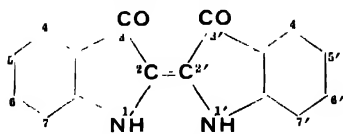
to two, five or six membered, unsaturated cyclic systems. By reduction of the two keto groups the system assumes the form



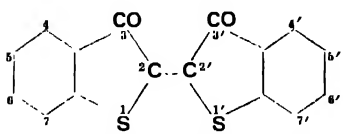
representing the "leuco-" compound, which is soluble in alkali and has dyeing properties. The molecule of the original dyestuff consists of two distinct cyclic systems, which may be alike or unlike, joined by the ethylenic double bond. Obviously the number of types of compound coming under the above definition is very large; and when it is remembered that substituent groups of all kinds can be introduced in every possible way it can be seen that thousands of different dyestuffs are possible.

The 7th edition of Schultz' Farbstofftabellen (1931) gives the constitution of 54 different commercial indigoid dyestuffs; there are in addition many of undisclosed constitution on the market, and hundreds are described in the patent literature.

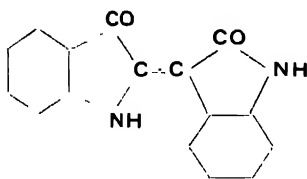
Indigoid dyestuffs are named from the ring systems from which the two portions of the molecule joined by the ethylene linking are derived. The following are the formulae and names of indigos which may be regarded as the parents of some dyestuffs of technical importance; others follow the same lines:



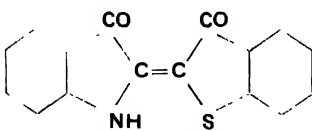
2,2'-Bis-indoleindigo (Indigotin).



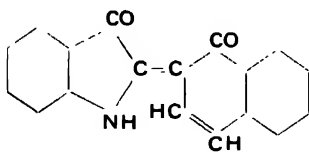
2,2'-Bis-thionaphthenindigo (thioindigo).



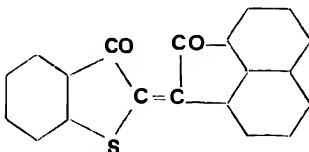
2,3'-Bis-indoleindigo (indirubin).



2-Indole-2'-thionaphthenindigo.



2-Indole-2'-naphthaleucindigo



2-Thionaphthalen-acenaphtheneindigo.

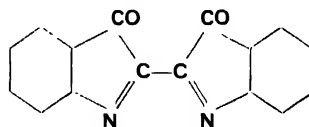
Note that three structural isomers are possible when the two components of the indigo molecule are alike, and four when they are unlike. Thus bis-indoleindigo has three isomers, indigotin (2,2'), indirubin (2,3') and *is*indigo (3,3'). The 2,2'-compounds are the deepest coloured and most important; the 3,3'-compounds are usually of little or no value as dyestuffs.

**Symmetrical Bis-Indoleindigos.**—Indigo-in has been dealt with fully in the article INDIGO, NATURAL and SYNTHETIC. Indirubin is of no technical importance. The halogenated indigotins, however, supply very valuable commercial dyestuffs, especially those containing bromine. The purple of the ancients, obtained from species of mollusc, *Murex brandaris* and *Murex trunculus*, was shown by Friedländer to be 6,6'-dibromoindigotin. It has never been manufactured synthetically. Bromination in the 6,6'-positions gives a product redder than indigotin, but halogenation in the 5- or 7-positions makes the shade a slightly greener blue, and brighter; halogenation in the 4,4'-positions is said to impart a much greener shade.

The commercial halogenated indigotins are manufactured by direct halogenation. "*Indigo Ciba R*" is a mixture of mono- and dibromoindigotins (5- and 5,5'-), which may be obtained by the action of bromine on dry indigo, or on a suspension of indigo in acetic acid, in sulphuric acid, etc. More highly brominated products are obtained by brominating in nitrobenzene solution (a process discovered by Engi), or under other conditions in which water is excluded. The most important of the products so obtained is 5,5':7,7'-tetrabromoindigotin, marketed as *Durindone Blue 4BC* (Imperial Chemical Industries), "*Ciba Blue 2B*" (Society of Chemical Industry, Basle), "*Indigo MLB/4B*," etc. The importance of these dyestuffs lies in the much greater affinity of the vat for all fibres than that of indigo itself.

Higher brominated indigotins, up to penta- and hexabromo-, can be obtained by the action of bromine on indigotin, or on lower brominated indigotins, in concentrated or in fuming sulphuric acid. "*Ciba Blue G*" is pentabromoindigotin.

Halogens also have the power of converting indigotin into dehydroindigotin by dehydrogenation, and, since dehydroindigotin is more readily halogenated than indigotin itself, the process can be continued to give highly halo-



Dehydroindigotin.

genated products. Thus by the action of chlorine on indigo in acetic acid in presence of anhydrous sodium acetate at 30°, tetrachloro-dehydroindigotin can be obtained. This with sodium bisulphite gives a compound which is hydrolysed by acid to tetrachloroindigotin and sodium hydrogen sulphate.

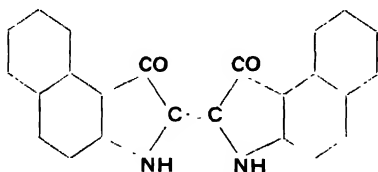
Other halogenated indigotins on the market are "*Brilliant Indigo BASF/B*" (5,5':7,7'-tetrachloro-), *BASF/2B* (5,5'-dichloro-7,7'-dibromo-), *BASF/G* (4,5,4':5'-tetrachloro-) and *BASF/4Q* (4,4'-dichloro-5,5'-dibromoindigotin).

The sole derivative of indirubin which has been marketed, as far as is known, is "*Ciba Heliotrope B*" (S.C.I.), probably a tetrabromoindirubin.

Two homologues of indigotin are known to have been marketed, the 7:7'- and 5:5'-dimethyl-indigotins, respectively "*Methylindigo B* and *R*." These may be obtained from *o*- and *p*-tolylglycine by the Heumann synthesis, or perhaps from the respective nitrotolualdehydes and acetone by the Baeyer synthesis (*v. INDIGO, SYNTHETIC*, this Vol., p. 443c).

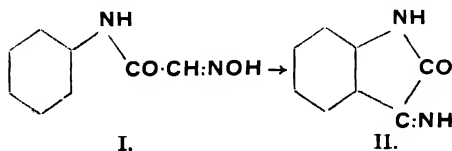
Nitro-derivatives of indigotin can be obtained by direct nitration if care be taken to exclude water; and also by other synthetic methods, *e.g.* reduction of nitroisatin chloride with hydrogen iodide. By reduction in the vat they give leuco-derivatives of aminoindigotin, which can also be obtained by direct synthesis, *e.g.* from aminophenylglycine. Only one amino-derivative has been used technically, "*Ciba Brown R*," which is 5:7:5':7'-tetrabromo-6:6'-diaminoindigotin. For recent work on the nitration of indigotin, see J. van Alphen, *Rec. trav. chim.* 1938, **57**, 837.

Many other substituted indigotins containing other groups such as hydroxyl, alkoxy, carboxyl, cyano-, mercapto-, etc., have been described in the scientific and patent literature, but none of the bis-indoleindigos of this kind are of technical interest. Four symmetrical indigos derived from naphthalene are possible and all are known. One of them, bis- $\beta$ -naphthindole-indigo is of some importance, since when brominated it gives a very bright green vat dye, used in print-



ing and marketed as "*Ciba Green G*" and "*Helindone Green G*."

**Asymmetrical Bis-indoleindigos.**—Substituted indigotins in which the two sides of the molecule are different are obtained by condensing an indoxyl with an isatin-2-chloride or isatin-2-anil. The isatins themselves condense with indoxyls to give dyes of the indirubin type, since the 3-keto-group of the isatin alone is active. If isatin-2-anil (or isatin chloride) is used, however, condensation gives an indigotin derivative. Isatin-2-anil is obtained by the method of Sandmeyer described under *INDIGO, SYNTHETIC* (this Vol., p. 446b). Another general method for producing isatins, also due to Sandmeyer (*Helv. Chim. Acta*, 1919, **2**, 234) is as follows. An aromatic amine, such as aniline, is boiled with a solution of hydroxylamine sulphate and chloral hydrate whereby oximinooacetanilide (I) is formed, which when merely dissolved in concentrated sulphuric acid is converted into isatin-3-imide (II) and this yields isatin on heat-

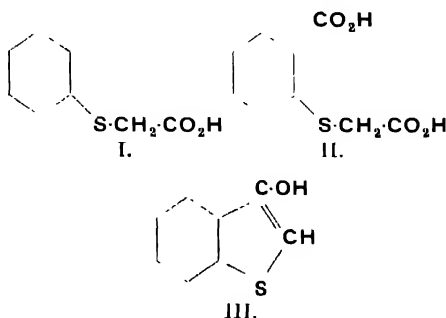


ing and diluting the solution. In this way Sandmeyer prepared many substituted isatins from the corresponding substituted anilines.

**Thioindigo and Derivatives.**—The discovery that a coloured compound of similar structure to indigotin could be obtained in which sulphur atoms were substituted for the imino-groups of the latter, was made by P. Friedlander (*Ber.* 1906, **39**, 1060). The resulting dyestuff is bright red, is readily vatted, and in the form of its leuco-compound has good affinity for textile fibres.

The methods of synthesis of thioindigo and its congeners are closely parallel to some of those employed for indigotin. The following is a brief description of a few of these methods.

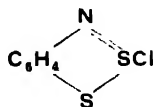
Phenylthioglycolic acid itself (I) can be cyclised to *thioindoxyl* (3-hydroxythionaphthen



(III)), but in practice, *o*-carboxyphenylthioglycolic acid (II) is used. Anthranilic acid is converted through its diazo-compound by the standard method into thiosalicic acid, this is condensed with chloroacetic acid to give (II), which is known technically as *O Acid*. The cyclisation proceeds more readily with these compounds than with the phenylglycines, and (II) is readily converted into thioindoxyl by baking with caustic soda in a vacuum at about 205°. Thioindoxyl is more stable than indoxyl, and although it can be oxidised to thioindigo by means of air, in practice a more rapid oxidation process is employed. Technically, the oxidation is accomplished by boiling a caustic soda solution of thioindoxyl with sulphur, or even by the action of molten sulphur on the thioindoxyl.

Thioindoxyl is a crystalline substance, m.p. 71°, very similar in odour and general properties to *a*-naphthol.

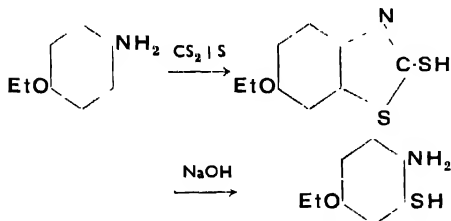
The *o*-aminothiophenols achieved importance as starting materials for the manufacture of thioindigoid dyes; a new and convenient method of preparing them was discovered by R. Herz, of L. Cassella & Co., in 1914. The method consists in a reaction between an aromatic amine and sulphur chloride,  $\text{S}_2\text{Cl}_2$ ; a compound of the type



is formed, which can be decomposed by alkali to give the *o*-aminothiophenol. If the *p*-posi-

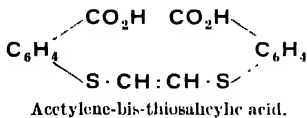
tion of the amine is free, chlorine substitution occurs in this position during the reaction with sulphur chloride. The *o*-aminothiophenol is condensed with chloroacetic acid to form the *o*-aminophenylthioglycolic acid, which is converted by the diazo reaction into *o*-cyanophenylthioglycolic acid, whence the *o*-carboxy-compound can be obtained. The route to the thioindigo is then as before. This method can be employed for obtaining a beautiful pink dye-stuff from *o*-toluidine, and an orange from *p*-phenetidine (see B.P. 17417, 18292/1914; G.P. 360690, 367344, 367345, 370854).

*o*-Aminothiophenols can also be obtained by a method discovered by A. W. Hofmann (Ber. 1887, 20, 1790), by fusing 2-mercaptobenzothiazoles with caustic alkali. This process has been applied by Du Pont de Nemours & Co. of America for preparing the orange thioindigoid dye from *p*-phenetidine. The base is converted into 6-ethoxy-2-mercaptobenzothiazole by heating with carbon disulphide and sulphur in an autoclave at 200°, and the mercapto-compound on fusion with caustic soda at 180–185° is converted into 2-amino-5-ethoxythiophenol (B.P.



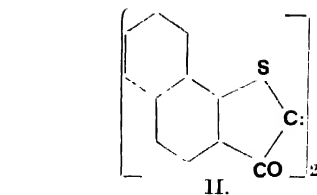
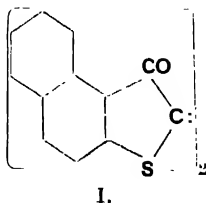
423869). The route to the thioindigoid dye is then as described above.

Two other methods of obtaining symmetrical thioindigoid dyes may be mentioned. When a salt of thioisacrylic acid reacts with *s*-dichloroethylene in presence of alkali, acetylene-bis-thioisacrylic acid is formed,



This is converted into thioindigo by treatment with a condensing agent such as sulphuric or chlorosulphonic acid (E. Munch, Z. angew. Chem. 1908, 21, 2059; G.P. 205324).

K. Dziewoński *et al.* (Bull. Acad. Polonaise, 1930, A, 198) discovered that  $\alpha$ - and  $\beta$ -naphthyl methyl ketone can be converted into 1:2-naphththioindigotin (I) and the 2:1-isomer (II) respectively by heating with sulphur at 230–260°:

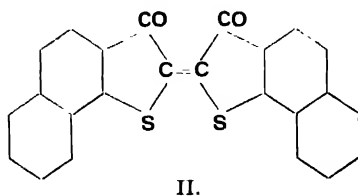
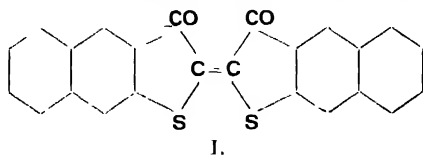


The brown dyestuff (I) can also be prepared by heating  $\beta$ -naphthylthioglycolic acid, and is of commercial importance. Acetophenone does not give *Thioindigo Red* in appreciable amount by this process (see T. W. Jezierski, Roczn. Chem. 1934, 14, 216).

**Properties of Thioindigo.**—Pure thioindigo is a solid substance which crystallises from organic solvents in reddish-brown crystals having a metallic lustre. It sublimes without melting when heated. Its solutions in chloroform, carbon disulphide and toluene show a magnificent reddish-yellow fluorescence but in alcoholic solutions only at the temperature of liquid air. It dissolves with a bluish-green colour in concentrated sulphuric acid with formation of a sulphate, and is sulphonated by fuming sulphuric acid at 30–40°. Many methyl-substituted thioindigos are known, including 4:5:7:4':5':7'- and 4:6:7:4':6':7'-hexamethyl derivatives.

Thioindigo is more readily reduced to the leuco-compound than indigo, and, unlike the latter, is reduced by sodium sulphide and even by sulphur dioxide. The leuco-compound is less readily oxidised and, therefore, more stable in air than leucoindigo. It can be isolated as pale yellow crystals, sparingly soluble in water; or as the sodium or magnesium salt. Thioindigo is also more stable to both oxidising agents and concentrated alkalis than indigo.

The effect on shade of substitution in the thioindigo molecule is similar to that in indigotin. Methyl, halogen or alkoxy in the 5- and 7-positions have a bathochromic effect, changing the shade from red towards violet; in the 6-positions the effect is hypsochromic, giving pink to orange shades. Thioindigos cover a greater range of shades than indigos. Thioindigos derived from naphthalene are of many possible types; they may be symmetrical or asymmetrical. It is interesting that dyes of the linear type (I) are bluish-green in colour, whilst those of angular type, such as (II), are brown. Com-



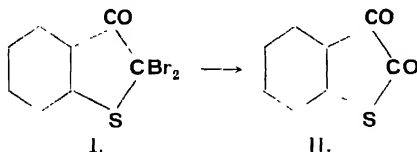


pounds of the hybrid type, half of (I) and half of (II), are dark blue. Similarly, the linear symmetrical dye from anthracene is green, the angular dyes brown. The linear dye from anthraquinone is said to be grey-blue, the angular brownish-grey.

The following are some of the commercial symmetrically substituted thioindigoid dyes: "*Ciba Bordeaux*" (5:5'-dibromo-); "*Ciba Red B*" (6:6'-dichloro-); "*Durindone Pink FF*" (6:6'-dichloro-4:4'-dimethyl-); "*Durindone Orange R*" (6:6'-diethoxy-); "*Helindone Red 3B*" (5:5'-dichloro-7:7'-dimethyl-); "*Helindone Fast Scarlet R*" (5:5'-dibromo-6:6'-diethoxy-); "*Indanthrene Grey 6B*" (7:7'-diamino-); "*Helindone Grey BR*" (5:5'-dichloro-7:7'-diamino-); "*Helindone Orange D*" (5:5'-dibromo-6:6'-diamino-2:2'-bisthionaphthenindigo).

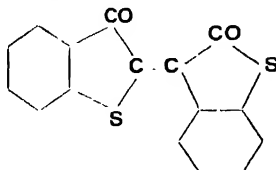
The Ciba dyes are manufactured by the Society of Chemical Industry, in Basle; Durindone dyes by Imperial Chemical Industries Limited, and Helindone and Indanthrene Dyes by I.G. Farbenindustrie A.-G. The last firm reserves the name "*Indanthrene*" for dyes of the highest fastness, and several indigoid dyes come into this category. Most of the dyes quoted are made by more than one firm, although only one name is given here.

**Thionaphthenquinones (Thioisatins).**—Corresponding with isatins in the indole series are the thionaphthenquinones or thioisatins in the thionaphthen series. Thionaphthenquinone (II) can be obtained by brominating thioindoxyl to the 2:2-dibromothioindoxyl (I) and hydrolysing. It forms intense yellow prisms, m.p. 121°.



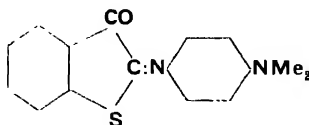
With aniline the dibromo- (or dichloro-) compound gives the 2-anil of the quinone.

When thioisatin condenses with, for example, a thioindoxyl, it reacts in the 3-position, just as isatin does, giving a dyestuff of indirubin type. Thus Friedlander (Monatsh. 1908, 29, 373) condensed thioisatin with thioindoxyl to form "thioindirubin,"



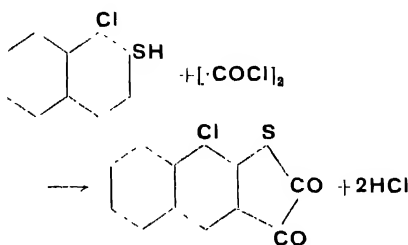
When, however, a 2-anil or 2-chloride of thioisatin is used for condensation, a dye of true indigoid type is obtained. There are unconfirmed statements in patents, however, that thioisatin itself will condense in the 2-position, e.g. with acenaphthenone (see G.P. 226244, Society of Chemical Industry in Basle), or with oxindole (G.P. 241327, Kalle & Co.), and the matter is, therefore, in an undecided state.

Anils of the thionaphthenquinones can also be obtained by the action of aromatic nitroso-compounds on thioindoxyl. From *p*-nitrosodimethylaniline and thioindoxyl, the *p*-dimethylaminoanil (below) is readily obtained, and frequently figures in the patent literature as an



intermediate for the preparation of indigoid dyes of many kinds (see B.P. 17498/1908, B.A.S.F.; also Pammetter, Ber. 1910, 43, 1370).

Thioisatins, especially naphththioisatins, are also obtained by condensing a thionaphthol with oxalyl chloride (B.P. 214864, Society of Chemical Industry in Basle), thus:



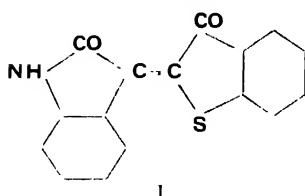
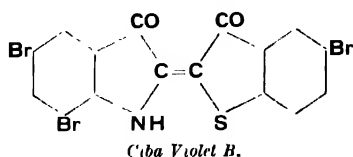
There do not appear to be any commercial examples of asymmetric thioindigoid dyes, although during the last 20 years a great many have been patented by German and Swiss firms.

**Selenoindigos.**—Dyestuffs similar to the thioindigoid dyes and the thiophenindole-indigos are known in which selenium is present in place of sulphur. Phenylselenoglycolic-o-carboxylic acid is cyclised by acetic anhydride (not by caustic alkali) to 3-hydroxyselenonaphthen, m.p. 76-77°, which is stable in air. In alkaline solution it reddens in air and is readily oxidised by potassium ferricyanide to selenoindigo. This is reddish-violet in colour, sublimes without decomposition at 270° giving a violet vapour, and can be vatted and dyed like thioindigo. Asymmetric indigoid dyes can be prepared from 3-hydroxyselenonaphthen, or from selenonaphthenquinone (a stable, red compound, m.p. 102-103°).

**Indigoid Dyes of Mixed Types.**—Just as isatinanilide will react with an indoxyl to give an indigoid dye, so it will react with a thioindoxyl to give a mixed indolethionaphthen-indigo, and conversely a thioisatinanilide will react with an indoxyl. More generally, the 2-chlorides and 2-anilides of both isatin and thioisatin will react with compounds containing reactive methylene groups, and by this reaction many new indigoid dyes are obtained. Such dyes can also be obtained by the interaction of cyclic 1:2-diketones with indoxyls and thioindoxyls.

2-Indole-2'-thionaphthenindigo is a violet dye of no interest because of its lack of fastness, but its 5:5'-dibromo-derivative is "*Ciba Violet 3B*,"

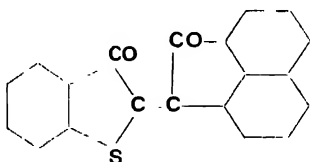
and a tribromo-derivative is "*Ciba Violet B.*" It should be noted that the shade is intermediate



between those of indigotin and thioindigotin.

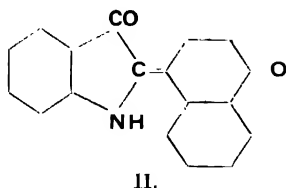
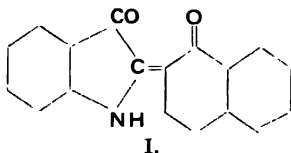
By condensing thioindoxyl with isatin a scarlet dyestuff (I), an analogue of indirubin, is obtained.

One of the most important dyes of this mixed series is obtained by condensing thioindoxyl with acenaphthenequinone, it has the formula



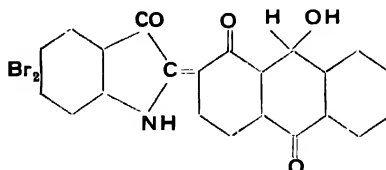
and is marketed as "*Ciba Scarlet G*" and "*Durindone Scarlet Y.*" A dibromo-derivative is "*Ciba Scarlet R.*"

Another type of indigoid dye is obtained by condensing isatin-2-chloride or -2-amide with  $\alpha$ -naphthol or  $\alpha$ -anthrol. P. Friedländer first discovered that indigoid dyestuffs could be obtained in this way (Ber. 1908, 41, 772). With  $\alpha$ -naphthol two products are obtained in about equal amounts, (I) and (II), but only (I) has the true indigoid structure. Dyes of type



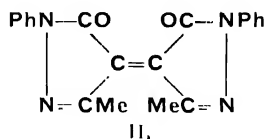
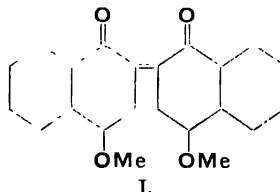
(II) are designated *indolignones*, this example being named 2-indole-1'-naphthalene-indolignone. F. Bayer & Co. condensed bromoisatin- $\alpha$ -chloride, and also brominated  $\beta$ -naphthisatins,

with  $\alpha$ -naphthol and  $\alpha$ -hydroxyanthracene in this way (G.P. 237199), and Meister, Lucius und Brüning, using  $\alpha$ -hydroxyoxanthrone instead of  $\alpha$ -hydroxyanthracene, obtained a dyestuff of presumably the following structure:



"*Helindone Blue 3GN*" is said to be a dye of this formula, whilst the above Bayer patent is said to cover "*Alizarin Indigo 3R*" and "*G.*"

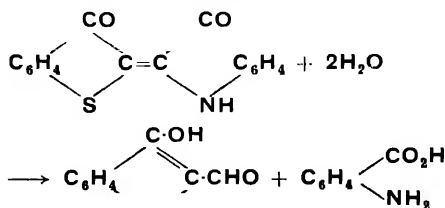
Mention may also be made of one or two dyes which fall into the indigoid class although containing neither an indole nor a thionaphthen residue. By oxidation of 4-methoxy- $\alpha$ -naphthol by ferric chloride, F. Russig (J. pr. Chem. 1900, [ii], 62, 53) obtained a blue dyestuff, having the formula (I), which can be dyed like indigo from a



vat. The I.G. Farbenind. A.-G. have patented a process of dyeing fur in fast blue shades by oxidising 4-methoxy- $\alpha$ -naphthol on the fur to this dyestuff (B.P. 407066). Another dye of indigoid type, *Pyrazole Blue* (II) was discovered by Knorr (Annalen, 1887, 238, 171) who showed its similarity to indigo.

**Scission of Indigoid Dyes.**—Many indigoid dyes can be split by heating with alkali into two components the identification of which establishes the constitution of the dye.

The bis-indoleindigos give by this treatment 1 mol. of a 3-hydroxyindole-2-aldehyde and 1 mol. of an anthranilic acid derivative. A thionaphthen-indoleindigo gives the 3-hydroxythionaphthen-2-aldehyde and anthranilic acid thus:



2-Naphthalene-2'-indoleindigo gives 1-naphthol-2-aldehyde. Thioindigo is more resistant than indigo to alkali fusion. With alcoholic caustic potash it breaks up giving thioindoxyl, thionaphthenquinone and the thioindogenide of 3-hydroxythionaphthen-2-aldehyde. Some of the substituted thioindigos cannot be split in this way, the reaction being far from general.

**Solubilised Indigoid Dyes—Indigosols.**—Indigoid dyes can be converted into sulphate esters of their leuco-compounds by the processes devised by Bader and Sunder and by Scottish Dyes, Ltd., respectively, in the same way as indigotin itself (see Indigosols under INDIGO, SYNTHETIC, this Vol., p. 449c). Different dyes give esters of different stability, but many are stable enough to be used commercially, and they are sold under the generic names of "Indigosols" (*I.G.*) and "Soledons" (*I.C.I.*) both of which ranges include solubilised indigoid and anthraquinone vat dyes. For the description of these dyes and their application, see F. Peterhauser (*J. Soc. Dyers and Col.* 1927, **43**, 251), M. Bader (*Chem.-Ztg.* 1937, **61**, 741, 763) and W. Christ (*J. Soc. Dyers and Col.* 1938, **54**, 93). The use of these solubilised forms of vat dyes is continually extending. Whittaker and Wilcock, ("Dyeing with Coal Tar Dyes," 3rd ed., London, 1939, p. 172) state that it is their practice to make ever-increasing use of the Soledons and Indigosols in dyeing both viscose and cotton in the skein form on the roller type of skein-dyeing machine. Christ gives a list of 28 Indigosol dyes of which 21 appear to be indigoids, the remainder being solubilised anthraquinone vat dyes. The Indigosols from indigoid dyes are colourless or only faintly coloured, whilst those from anthraquinone vat-dyes are deeply coloured.

**Bibliography.**—J. Martinet, "Matières Colorantes. Les Indigoïdes," Paris, J.-B. Baillière et Fils, 1934. H. E. Pierz-David, "Kunstliche organische Farbstoffe," Berlin, 1926. Colour Index, edited by F. M. Rowe, 1924. Reports of Applied Chemistry, published by the Society of Chemical Industry, articles on Intermediates and Colouring Matters. For German patents, Friedländer, "Fortschritte der Teerfarbenfabrikation, 1877-1935," Theil. 1-22.

E. H. R.

**INDIUM.** At. no. 49; At. wt. 114.76. Indium belongs to the aluminium group of the elements and was discovered by Reich and Richter in 1863 during the spectroscopic examination of some crude zinc chloride from a Freiberg zinc blende (*J. pr. Chem.* 1863, [i], **89**, 441; **90**, 172; 1864, [i], **92**, 480). The name *indium* was chosen because of the prominence of the two indigo-blue lines in its spectrum. Although occurring only in small quantities it is, like many rare metals, widely distributed in nature and is found in numerous zinc blendes, pegmatites, siderites and in some tungsten, manganese and tin ores (Hartley and Ramage, *J.C.S.* 1897, **71**, 533; Brewer and Baker, *J.C.S.* 1936, 1286; Zomeya, *J. Amer. Chem. Soc.* 1933, **55**, 3899).

Extraction of indium is inevitably a tedious process which at some stage or other includes repeated or fractional electrolytic deposition of the metal. Separations from other metals are also based on: (a) the solubility of indium sul-

phide in 2-3*N.* hydrochloric or sulphuric acid and its insolubility in 0.5-0.8*N.* acid; (b) precipitation of indium sponge by means of zinc; (c) the insolubility of basic indium sulphite; (d) precipitation from alcohol of the complex between anhydrous indium chloride and pyridine; (e) sublimation of indium tribromide; (f) precipitation of indium hydroxide with ammonia in the presence of ammonium salts. The most difficult impurity to remove is iron, although small amounts of it may be separated by extracting as ferric thiocyanate with ether (Reich and Richter, *l.c.*; Lawrence and Westbrook, *Ind. Eng. Chem.* 1938, **30**, 611; Thiel, *Z. anorg. Chem.* 1904, **39**, 119; **40**, 290; Bayer, *Annalen*, 1871, **158**, 372; Mathers, *J. Amer. Chem. Soc.* 1907, **29**, 485; Dennis and Geer, *ibid.* 1904, **26**, 437; U.S.P. 1855455, 1886825, 2052387).

**Physical Properties.**—Indium is a silvery-white, readily malleable metal, ductile and softer than lead. It can be obtained crystalline, the X-radiogram indicating a face-centred tetragonal structure with 4 atoms per unit cell whose dimensions are  $a_0=4.583$  (4.588) Å.,  $c_0=4.936$  (4.946) Å.,  $a:c=1:1.077$  (1.078) (Zintl and Neumayr, *Z. Elektrochem.* 1933, **39**, 81; Dwyer and Mellor, *J. Proc. Roy. Soc. New South Wales*, 1932, **66**, 234; Frevet and Ott, *J. Amer. Chem. Soc.* 1935, **57**, 228); the atomic radius is 1.569 Å. (Goldschmidt, *Z. physikal. Chem.* 1928, **133**, 408), and the calculated density 7.308 (Z. and N.).

Two isotopes are known with masses 113 and 115, the relative abundances being 4.5 and 95.5%. For radioactive isotopes, see Lawson and Cork (*Physical Rev.* 1937, [ii], **52**, 531).

Indium has a comparatively low m.p. (155°C.) and high b.p. (1450°C.);  $d_{20}^{20}$  is 7.31. Polished surfaces of the metal possess a high reflecting power making it suitable for mirrors and reflectors.

Other physical properties are:

Compressibility (megabar $^{-1} \times 10^6$ ): 2.55 between 100 and 500 megabars pressure.

Hardness=1.0 Brinell. Tensile strength (99.71% metal)=15,980 lb. per sq. in.

Average specific heat between 0° and 154° is given by  $c_p=0.0569+0.000013(t-18)$  g.-cal. per g.

Specific resistance (ohm-cm.  $\times 10^6$ ): 9 at 20° and 29 at 155°. The mean temperature coefficient between 0° and 100° is  $490.4 \times 10^{-6}$ . Indium becomes superconducting at low temperatures.

**Spectra.**—Indium compounds colour the Bunsen flame a bluish-red while the flame, arc and spark spectra show two brilliant indigo-blue lines of wave-lengths 4101.8 and 4511.3 Å. respectively. Other prominent lines in the arc spectrum are 2710.25, 3039.36 and 3256.06 Å. Lines due to singly and doubly ionised indium have also been mapped (Paschen, *Ann. Physik*, 1938, [v], **32**, 148).

For the X-ray spectrum, see Blake and Duane (*Physical Rev.* 1917, [ii], **10**, 697), Valasek (*ibid.* 1929, [ii], **34**, 1231) and Siegbahn (*Jahrb. Radioaktiv.* 1916, **13**, 206).

**Chemical Properties.**—Indium reacts as a tri-, di- and mono-valent element, this being also the order of stability of its compounds so that only

those of the trivalent series are stable in aqueous solution. The metal is unaffected by air at ordinary temperatures and is not attacked by boiling water or alkalis. Heated to redness in air or oxygen it burns with a blue flame producing the trioxide; sulphur, selenium and tellurium also combine with the heated metal, incandescence occurring in each case (Thiel and Kocksch, *Z. anorg. Chem.* 1910, **66**, 315). Halogens react readily on warming. Indium is slowly soluble in cold and more readily so in hot dilute mineral acids; the attack of concentrated acids is more vigorous.

#### ALLOYS.

Numerous alloys containing indium have been produced largely with the desire to secure dental alloys, to impart corrosion-resistance to metals like silver and copper or to obtain fusible alloys. Indium amalgamates with mercury, and dental amalgam bases containing up to 50% indium have been patented (U.S.P. 1959668).

The silver-indium system has been closely studied, but the hope that such alloys might possess tarnish resistance has not been fulfilled. Over 40% of indium is necessary to provide a completely tarnish-proof product and such alloys are too hard and brittle to be of practical importance. Better results are claimed by plating the metal on to silver, but difficulties have been experienced through dull coatings and inability to secure a good polish. The addition of small amounts of indium to the precious metals improves their colour, hardness and strength. Some of the many alloys which have been made with copper possess precipitation- and heat-hardening properties (Weibke *et al.*, *Z. anorg. Chem.* 1934, **220**, 273; 1937, **231**, 197).

Indium has been recommended as a constituent of bearing-metals, in order to increase the resistance to attack by organic acids derived from vegetable lubricating oils (B.P. 283862). Low-melting alloys are obtained by adding indium to Wood's metal, the reduction in the melting-point of the latter being proportional to the concentration of the rare metal, reaching a maximum with 18% indium, this alloy melting at 46.9°C.

Alloys have also been produced with magnesium, zinc, cadmium, gallium and lead as well as with the alkali metals.

#### SALTS.

**Indium Trifluoride,  $\text{InF}_3$ .**—Obtained as a white powder by heating ammonium indium fluoride  $(\text{NH}_4)_3\text{InF}_6$ , or indium sesquioxide in a stream of fluorine; it melts at 1170° and has  $d_4^{25}$  4.39. It is very sparingly soluble in hot and cold water, yielding a slightly acid solution; in dilute acids it dissolves readily (Hannebohn and Klemm *Z. anorg. Chem.* 1936, **229**, 337).

Evaporation of a solution of the sesquioxide in hydrofluoric acid apparently gives either tri- or ennea-hydrated fluoride according, presumably, to the temperature of crystallisation. The trihydrate when treated with liquid ammonia yields the triammine  $\text{InF}_3 \cdot 3\text{NH}_3$  (Thiel, *Z. anorg. Chem.* 1904, **40**, 280; Klemm and Kilian, *ibid.* 1939, **241**, 93; Chabrie and Bouchonnet, *Compt. rend.* 1905, **140**, 90).

**Indium Chlorides.**—The anhydrous tri-chloride  $\text{InCl}_3$  may be formed by the usual methods, purification being by distillation in a current of carbon dioxide. So obtained it appears as white, deliquescent, lustrous plates,  $d_4^{25}$  3.46, m.p. 586°. It volatilises readily above 600°, but at about 1100° dissociation to a lower chloride becomes evident. The chloride is lightly hydrolysed in aqueous solution, crystallisation from solution being difficult; evaporation of the solution at elevated temperatures is said to yield an insoluble oxychloride. *Indium oxychloride,  $\text{InOCl}$ ,* has been made by Thiel as a sparingly soluble white powder by passing a mixture of oxygen and chlorine over the dichloride.

Indium trichloride readily forms double compounds with alkali chlorides of the types  $\text{K}_3[\text{InCl}_6]$ ,  $\text{Rb}_3[\text{InCl}_6 \cdot \text{H}_2\text{O}]$ ; the cesium compound,  $\text{Cs}_3[\text{InCl}_6]$ , which readily separates as tetrahedra, has been recommended for use in a microchemical test for indium.

Ammoniates containing 7, 5, 3, 2 and 1 molecule of ammonia per molecule of the trichloride are known, while with pyridine in alcoholic solution there is produced a white crystalline precipitate of the complex  $\text{InCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$ . Double salts have been obtained with many other organic bases (Ekeley and Potratz, *J. Amer. Chem. Soc.* 1936, **58**, 907).

**Indium Dichloride** is formed as a yellow liquid, solidifying to white crystals on cooling, by heating indium, indium trichloride or indium sesquioxide in a current of dry hydrogen and hydrogen chloride, m.p. 235°, b.p. ~570°,  $d_4$  3.64. It is probably associated in the solid state, but between 500° and 700° it exists as undissociated simple molecules. In contact with water it decomposes into indium and indium trichloride. Aiken *et al.* (*Trans. Faraday Soc.* 1936, **32**, 1617) state that the action is one of disproportionation into  $\text{InCl}$  +  $\text{InCl}_3$  followed by the reaction  $\text{InCl} \rightarrow \text{In} + \text{InCl}_3$ . These authors regard the dichloride as being derived from the hypothetical "indichloric acid"  $\text{HInCl}_2$ , the decomposition in water being represented thus:



Reduction of the dichloride or trichloride by heating with the metal leads to the formation of indium monochloride,  $\text{InCl}$ , which is a dark-red solid,  $d_4^{25}$  4.18, melting to a blood-red liquid. As indicated above it is decomposed by water, yielding indium and indium trichloride (de Boisbaudran, *Compt. rend.* 1885, **100**, 701; Thiel, *l.c.*; *Ber.* 1904, **37**, 175; Nilson and Pettersson, *Z. physikal. Chem.* 1888, **2**, 657; Klemm and co-workers, *Z. anorg. Chem.* 1927, **163**, 225, 235, 240; 1934, **219**, 42; Robert and Wehrli, *Helv. Phys. Acta*, 1935, **8**, 322).

**Indium Bromides.**—The three bromides corresponding to the above chlorides have been prepared and resemble them in properties. The lower bromides are less easily decomposed by water, so that although the dibromide is readily converted into the tri- and mono-salts heating is necessary to change the latter into the metal and tribromide. Double compounds are formed

between the tribromide and alkali or ammonium bromides, while ammoniates containing 13, 7, 5 and 3 molecules of ammonia are known.

**Indium Iodides.**—Indium di-iodide has not definitely been isolated, but the tri- and mono-valent derivatives have been made. The *mono-iodide* is stable to hot water but dissolves in dilute acids with evolution of hydrogen (Thiel, *l.c.*; Z. anorg. Chem. 1910, **66**, 288; Klemm *et al.*, *l.c.*).

**Indium Sesquioxide,  $\text{In}_2\text{O}_3$ .**—Ignition of the hydroxide, carbonate, nitrate or sulphite at comparatively low temperatures yields a pale yellow amorphous oxide which, according to Renz (Ber. 1903, **36**, 1847), is converted into yellow, trigonal crystals, isomorphous with those of ferric oxide, on heating at high temperature in air. The two modifications differ considerably in their solubility in dilute acids, the crystalline form being so resistant that it can be separated from the amorphous variety by boiling with dilute sulphuric acid. Heated above  $850^\circ$  and without free access of air the sesquioxide begins to decompose slowly and then appears white, owing to a thin superficial film of the lower oxide  $\text{In}_2\text{O}$ . According to Thiel and Luckmann (Z. anorg. Chem. 1928, **172**, 353) the purest form of oxide is obtained by heating the hydroxide at  $850^\circ$  to constant weight and then heating in air at  $1000^\circ$  for half an hour. So prepared, its density is said to be 6.75–1.0.01, but Klemm and Von Vogel (*ibid.* 1934, **219**, 45) give it as 7.04 while other values up to 7.18 have also been reported.

**Indium Hydroxide,  $\text{In}(\text{OH})_3$ .**—White, colloidal precipitate produced when solutions of indium salts are treated in the cold with aqueous ammonia, alkalis or hydroxylamine; heating the mixture or precipitating from hot solutions yields a dense, granular precipitate. The freshly deposited amorphous form is slightly soluble in excess of ammonia and readily so in excess of alkali hydroxide; reprecipitation occurs on boiling or adding ammonium salts. Both the colloidal and granular forms show the same X-ray diffraction pattern and are the hydrous trihydrate or hydroxide (Weiser and Milligan, J. Physical Chem. 1936, **40**, 1; J. Amer. Chem. Soc. 1937, **59**, 1670).

In addition to its basic properties, indium hydroxide also possesses weakly acid functions; the product obtained by careful drying at about  $150^\circ$ , which has the composition  $\text{InO}(\text{OH})$ , may tautic acid,  $\text{HInO}_2$ . A magnesium metatmate,  $\text{Mg}(\text{InO}_2)_2 \cdot 3\text{H}_2\text{O}$ , was obtained by Renz (Ber. 1901, **34**, 2763) by boiling a solution of indium and magnesium chlorides; the white powder so produced is insoluble in water but dissolves in dilute acids.

**Lower Oxides of Indium.**—Winkler stated that on heating the sesquioxide in hydrogen at  $300^\circ$  a black oxide,  $\text{In}_2\text{O}_4$ , was formed, while the preparation of intermediate oxides,  $\text{In}_2\text{O}_6$ ,  $\text{In}_4\text{O}_6$ , etc., was also claimed. Thiel and Luckmann (*l.c.*) found, however, that there was no interaction at  $300^\circ$ , but that at  $500^\circ$  a bluish-black material was formed consisting of crude  $\text{In}_2\text{O}$ . This substance could be purified by subliming in a high vacuum at a temperature of  $650$ – $700^\circ$ , and in thin transparent films had a

yellow colour although thicker layers formed a black, brittle and fairly hard mass of density 6.34 (Thiel and Luckmann) or 6.99 (Klemm and Von Vogel). This oxide is stable to cold water but dissolves in hydrochloric acid with evolution of hydrogen. Heated in air it glows suddenly and is converted into  $\text{In}_2\text{O}_3$ ; it does not melt below  $1000^\circ$ .

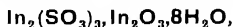
The residue left after subliming the  $\text{In}_2\text{O}$  is a dirty-white powder the composition of which agrees with the formula  $\text{In}_2\text{O}$ , but it has not been obtained sufficiently pure for its identity as an oxide of bivalent indium to be established.

**Indium Sesquisulphide,  $\text{In}_2\text{S}_3$ .**—Prepared by heating the metal with excess sulphur, by passing hydrogen sulphide over the heated oxide or by precipitation with alkali or hydrogen sulphide from neutral or faintly acid solutions of indium salts; in the last method it is necessary to remove excess of sulphur by heating the product in an indifferent gas. According to the method of preparation it is yellow to brown in colour. It is appreciably volatile at  $850^\circ$ , but some decomposition takes place as the sublimate contains free sulphur and a brownish-black substance, presumably  $\text{In}_2\text{S}$ . Heated in a sealed tube the sesquisulphide melts at  $1050^\circ$ , the melt solidifying on cooling to a black mass, density 4.89, which is red when finely divided. The sulphide dissolves in concentrated acids and is converted to the oxide on roasting in air. Double salts,  $\text{KInS}_2$  and  $\text{NaInS}_2 \cdot \text{H}_2\text{O}$ , have been made.

**Lower Sulphides of Indium.**— $\text{In}_2\text{S}$  is formed by subliming *in vacuo* the crude slate-grey material obtained by heating indium with a slight excess of the theoretical amount of sulphur at  $450^\circ$  in carbon dioxide. It is yellow in thin layers but thicker films are black with a metallic lustre; m.p.  $653^\circ$ ,  $d_4^{25}$  5.951 (5.87).

Sublimation *in vacuo* at  $850^\circ$  of the product made by heating molecular proportions of indium and sulphur yields only  $\text{In}_2\text{S}$  and S. The slate-grey colour of the crude material differs from that of the reddish-brown, soft mass formed by passing hydrogen sulphide over the heated metal and which Thiel and Koelsch (Z. anorg. Chem. 1910, **66**, 314) stated was  $\text{InS}$ . Klemm and Von Vogel (*l.c.*) give 5.18 as the density of this sulphide (Meyer, Annalen, 1869, **150**, 137; Thiel, *l.c.*; Thiel and Luckmann, *l.c.*).

**Indium Sulphite.**—A basic sulphite,



is obtained as a crystalline powder on boiling a solution of an indium salt with sodium bisulphite.

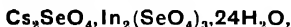
**Indium Sulphate,  $\text{In}_2(\text{SO}_4)_3$ .**—Concentration of a solution of the metal or hydroxide in a large excess of sulphuric acid yields diamond-shaped crystals of an acid indium sulphate,  $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ . The salt is stable under ordinary conditions but evolves sulphuric acid above  $250^\circ$  leaving a residue of the anhydrous normal sulphate. Slow evaporation of an aqueous solution of this residue leads to the separation of small prismatic crystals of  $\text{In}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ . Addition of alcohol to the aqueous solution precipitates a basic salt,  $\text{In}_2\text{O}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Seward, J. Amer. Chem. Soc. 1933, **55**, 2740).

A number of double sulphates have been prepared, including the ammonium, rubidium and caesium alums,  $M_2SO_4 \cdot In_2(SO_4)_3 \cdot 24H_2O$  ( $M = NH_4, Rb$  or  $Cs$ ). These crystallise in the usual regular octahedra and have low melting-points, that of the rubidium salt being  $42^\circ$  and of the ammonium alum  $36^\circ$  ( $37-38^\circ$ ). Solutions of the alums react acid and deposit basic sulphates or indium hydroxide on heating.

The sodium and potassium alums have not been made, but double sulphates of the type  $Na_2SO_4 \cdot In_2(SO_4)_3 \cdot 8H_2O$  are known, as are also the corresponding thalious and ammonium compounds. The ammonium double salt is the stable modification above the melting-point of the ammonium indium alum in the system  $(NH_4)_2SO_4-In_2(SO_4)_3-H_2O$ . The melting-point of the alum is also the transition point. Double salts with certain organic bases have been made (Reich and Richter, *l.c.*; Meyer, *l.c.*; Nilson and Pettersson, *Compt. rend.* 1880, **91**, 232; Chabré and Rengade, *ibid.* 1900, **131**, 1300; 1901, **132**, 472; Roessler, *J. pr. Chem.* 1873, [ii], **7**, 14; Soret, *Arch. Sci. phys. nat.* 1885, [iii], **13**, 5; 1888, [iii], **20**, 520; Hattox and De Vries, *J. Amer. Chem. Soc.* 1936, **58**, 2126; Ekeley and Potratz, *ibid.*, p. 907).

**Selenium and Tellurium Compounds of Indium.**—A complete range of tri-, di- and mono-valent selenides and tellurides has been obtained by synthesis while the sesquiselenide  $In_2Se_3$  is also formed as a brown precipitate on passing hydrogen selenide into a solution of indium acetate (Thiel and Koelsch, *l.c.*; Klemm and Von Vogel, *l.c.*).

Hydrated selenites and selenates have been prepared, and the formation from the selenate of a caesium selenium alum,



has been reported although this compound is said to crystallise in tetragonal pyramids (Mather and Schluederberg, *J. Amer. Chem. Soc.* 1908, **30**, 215).

**Indium Nitride,  $InN$ .**—Said to be formed on heating ammonium indium fluoride at  $600^\circ$ . X-ray analysis indicates that it has an hexagonal, wurtzite lattice, the calculated density being 6.91 (Juza and Hahn, *Z. anorg. Chem.* 1938, **239**, 282; *Angew. Chem.* 1938, **51**, 189).

**Indium Nitrate.**—A solution of indium nitrate produced by dissolving the metal, oxide, hydroxide or carbonate in nitric acid deposits crystals on concentration with greater difficulty the more nearly neutral is the solution. In the presence of nitric acid the hydrate  $In(NO_3)_3 \cdot 4H_2O$  separates fairly readily as colourless, deliquescent needles readily soluble in water; this salt loses two-thirds of its water of crystallisation when heated at  $100^\circ$ . Attempts at complete dehydration, using higher temperatures, result in some decomposition of the nitrate (Winkler, *J. pr. Chem.* 1867, [i], **102**, 292). A white double nitrate has been obtained with ammonium nitrate (Dennis and Geer, *J. Amer. Chem. Soc.* 1904, **26**, 437).

**Indium Carbonate.**—Addition of alkali carbonate to aqueous solutions of indium salts precipitates a white compound, insoluble in excess of precipitant but soluble in ammonium

carbonate solution. This precipitate is stated to be indium carbonate but the substance has not received careful study (Winkler, *J. pr. Chem.* 1867, [i], **102**, 273).

#### ORGANIC COMPOUNDS OF INDIUM.

**Indium Trimethyl,  $In(CH_3)_3$ .**—Obtained when indium, mercury dimethyl and a little mercuric chloride are heated together in dry  $CO_2$  at  $100^\circ$  for 8 days. Excess mercury dimethyl is distilled off and the residue purified by sublimation. The indium trimethyl forms colourless acicular crystals, m.p.  $89-89.5^\circ$ , which are easily decomposed by water, air or oxygen. Cryoscopic measurements in benzene indicate molecular association to  $[In(CH_3)_3]_4$  although it is monomeric in the vapour state (Dennis *et al.*, *J. Amer. Chem. Soc.* 1934, **56**, 1047; Laubengayer and Gilliam, *ibid.* 1941, **63**, 477).

**Indium Triphenyl,  $In(Ph)_3$ .**—Formed by heating indium and mercury diphenyl at  $130^\circ$  in a sealed tube, extracting the mass with chloroform, filtering and concentrating until colourless needles are obtained. Schumb and Crane (*ibid.* 1938, **60**, 306), carrying out the operations in an atmosphere of  $CO_2$ , found their product melted at  $291^\circ$  but Gilman and Jones (*ibid.* 1940, **62**, 2353) using nitrogen give  $208^\circ$  as the melting-point and, moreover, they show that indium triphenyl is slowly decomposed by  $CO_2$ . It also reacts with water, oxygen and a number of organic compounds. Successive addition of bromine leads to the formation of diphenylindium bromide, phenylindium dibromide and indium tribromide; similar reactions occur with iodine. The halogen derivatives are buff-coloured powders. Diphenylindium chloride and phenylindium oxide have also been reported (Goddard in Vol. XI of Friend's "Text-book of Inorganic Chemistry").

**Indium Acetylacetone,  $In(C_5H_7O_2)_3$ .**—Obtained by heating indium hydroxide with alcoholic acetylacetone and concentrating the solution. It is dimorphous, one form being isomorphous with  $\beta$ -gallium and scandium acetylacetones and the other with ferric acetylacetone. It can be sublimed at  $140^\circ$  under 10 mm. pressure; the melting-point is  $183^\circ$  (Chabré and Rengade, *Compt. rend.* 1900, **131**, 1300).

Numerous salts of organic acids have been made of which indium tartrate is said to possess preventive and curative properties against certain forms of experimental trypanosomiasis (Meyer, *l.c.*; Ekeley and Johnson, *J. Amer. Chem. Soc.* 1935, **57**, 773; Levaditi *et al.*, *Compt. rend.* 1932, **194**, 325).

G. R. D.

**INDOCYANINES** (Vol. I, 577d; Vol. III, 519c).

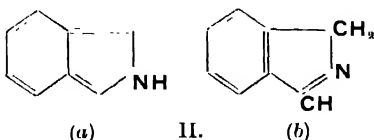
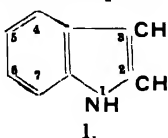
**INDOINE BLUE** (Vol. I, 576c).

**INDOLE** (as perfume). This body, a parent of the indigo group of compounds, is a liquid of powerful and disagreeable odour, but in minute quantities acts, like civet and skatole, as a strong fixer of perfumes, and the odour disappears on dilution. For its determination in essential oils, see Parry's "Chemistry of Essential Oils," Vol. II, p. 292.

E. J. P.

**INDOLENINE YELLOW** (Vol. III, 519d).

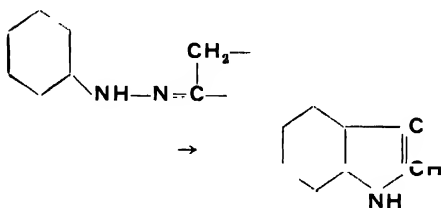
**INDOLES.** Compounds containing a 5-membered pyrrole ring fused to a benzene ring. Two structures are thus possible, indole and



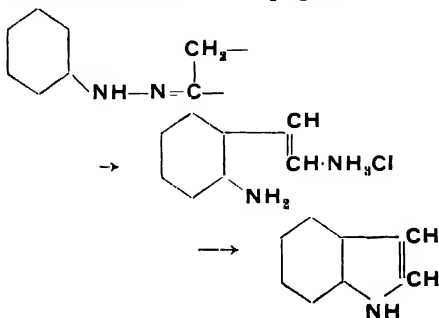
isoindole, (I) and (IIb) respectively; the second possibility is not encountered among simple compounds and even the isomeric pseudo-indole system (IIa) is unstable in its simple representatives.

The indole group is of considerable importance in natural economy—indigo, tryptophan and skatole are naturally occurring indoles—and becoming increasingly important in technical practice.

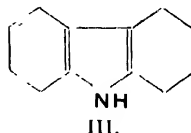
**General Syntheses.**—(1) The phenylhydrazones of carbonyl compounds containing the grouping  $\text{—CO—CH}_2\text{—}$  are treated with condensing agents such as zinc chloride, copper chloride or acid:



and the elimination of ammonia may in some cases be effected catalytically (Arbusow, Saizew and Rasumow, Ber. 1935, **68** [B], 1792). The reaction is thought to involve (1) the trans formation of the hydrazone into an unsaturated hydrazine; (2) the benzidine-type rearrangement of the resulting hydrazine; (3) ring formation by elimination of ammonium salt from the product (Robinson and Robinson, J.C.S. 1918, **113**, 639; 1924, **125**, 827; cf. Campbell and Cooper, *ibid.* 1935, 1208), although many other mechanisms had been proposed earlier:

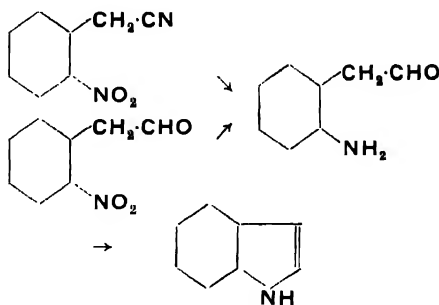


The reaction cannot be applied to the formation of indole itself, but the phenylhydrazone of acetone affords 2-methylindole in moderate yield. Generally the carbonyl component may be aldehydic or ketonic, even  $\alpha$ -ketoacids reacting in this way; a variety of substituted aryl hydrazines and secondary hydrazines have been employed, the reaction usually proceeding still more readily with the latter. When the ketonic compound is a cyclic ketone the final product is tricyclic; thus the phenylhydrazone of cyclohexanone yields 1:2:3:4-tetrahydrocarbazole (III). For recent applications of the synthesis,

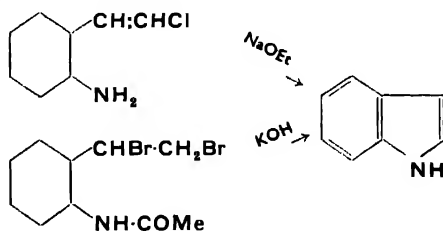


see Julian and Piki (Proc. Indiana Acad. Sci. 1936, **45**, 145); Moggridge and Plant (J.C.S. 1937, 1125); Hughes and Lyons (Proc. Roy. Soc. New South Wales, 1937-38, **71**, 475).

(2) Many synthetic reactions depend upon the internal reaction of an aromatic amine with a reactive ortho  $\text{—C—C—X}$  group. Thus reduction of *o*-nitrophenylacetonitrile, *o*-nitrophenylacetaldehyde (Stephens, J.C.S. 1925, **127**, 1874; Weerman, Annalen, 1913, **401**, 12) results in ring-closure. Indole is also formed by ring



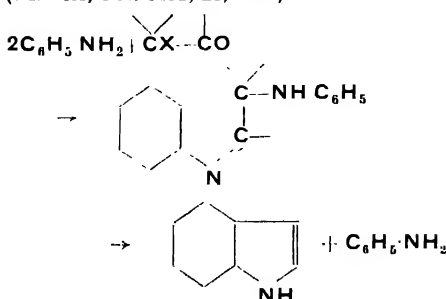
closure of *o*-amino- $\omega$ -chlorostyrene or *o*-acetaminostyrene dibromide (Lipp, Ber. 1884, **17**, 1072; Taylor and Hobson, J.C.S. 1936, 181):



(3) The calcium salt (Mauthner and Suida, Monatsh. 1889, **10**, 252), or better the alkali salts of phenylglycine, afford indole on fusion, preferably in presence of reducing agents (G.P. 152683).

(4) The reaction of aromatic bases with

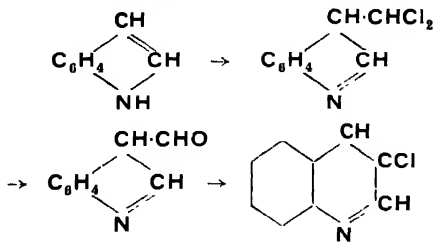
$\alpha$ -halogenated ketones is of general application (Bischler, Ber. 1892, 25, 2860):



A similar reaction is the production of indole by reducing *o*-dinitrostyrene with iron, zinc dust or aluminium amalgam (Van der Lee, Rec. trav. chim. 1925, 44, 1089). A recent method consists in nitrating phenylethyl chloride, reducing the *o*-nitro-compound with hydrosulphite and finally treating the amine with hexamethylene-tetramine (Russ. P. 48309).

**Properties.**—Indoles are feebly basic in nature and participate in most of the reactions of pyrroles although they are less sensitive than the simpler compounds. Thus they form alkali metal compounds (Weissberger, Ber. 1910, 43, 3521) and can be polymerised in contact with acids, tri-indoles being well characterised products (for constitution, see Schmitz-Dumont *et al.*, *ibid.* 1930, 63 [B], 323; 1933, 66 [B], 71; 1935, 68 [B], 240; J. pr. Chem. 1931, [n], 131, 146; 132, 39; 1934, [n], 139, 167; Annalen, 1933, 504, 1; 1934, 514, 267).

Towards strong substituting reagents indoles usually react abnormally, but with weaker reagents substitution occurs in the 3-position when that is free. Thus iodination or chlorination (using sulphuryl chloride; Pauly and Gundermann, Ber. 1908, 41, 4007; Mazzara and Borgo, Gazzetta, 1905, 35, n. 564, 566) affords 3-halogenoindoles and alkyl nitrites or nitrates yield 3-nitroso- or 3-nitro-derivatives (Angeli and Marchetti, Atti. R. Accad. Lincei, 1907, [v], 18, 1, 381; Angelico and Velardi, *ibid.* 1904, [v], 13, 1, 242). 1-Acetyl- and 1:3-diacetyl-indoles are obtainable by direct acetylation (Zatti and Ferratini, Ber. 1890, 23, 1359). Indoles undergo typical pyrrole reactions with chloroform and alkali to yield 3-formyl-indoles and, by intermediate rearrangement, 3-chloroquinolines:



(Ellinger, *ibid.* 1906, 39, 2520).

Indoles containing a free 3-position react with diazonium salts and also with Grignard com-

pounds, and from the products of the latter reaction 3-substituted indoles can be obtained. Aldehydes of the indole series are readily prepared by the action of methylformylanilide on indoles in the presence of a condensing agent (I.G. Farbenind., A.-G., F.P. 773259, 1933).

Indoles are readily hydrogenated first to 2,3-dihydroindoles (G.P. 623693), then to perhydroindoles and finally on drastic hydrogenation the 5-membered ring suffers fission with production of *o*-alkylanilines; this fission is less readily effected when the pyrrole ring is highly alkylated (see Von Braun and Bayer, Ber. 1925, 58 [B], 387).

Indole forms 2.5% of the oil extracted by fat from picked jasmine flowers, and 100 g. of the flowers liberate as much as 5–6 mg. of indole in a confined space (Cerighelli, Compt. rend. 1924, 179, 1193); it has also been detected in several other plant products, *e.g.* in "Jopgoza" oil (Madagascar) (Traubaud and Sabatay, Perf. and Essent. Oil Rec. 1938, 29, 142; see also Gildemeister and Hoffmann, "Die Aetherischen Oele," 3rd ed., Vol. I, p. 677). Indole is also found in coal tar (Weissgerber, Ber. 1910, 43, 3520), and together with skatole is a constant product of biological degradation of protein by pancreatic or bacterial digestion (*literature*: Ellinger in Abderhalden, "Handb. d. biol. Arbeitsmethoden," Abt. I, Teil 7, 1923, p. 779) and is therefore frequently found in products of animal origin, *e.g.* normal perspiration contains 0.003–0.05% of indole (Labhardt, Zentr. Gynak. 1924, 48, 2626) and sewage and sludge may contain 0.25 parts per billion and 0.8 p.p.m. respectively (Rudolfs and Ingols, Sewage Works J. 1938, 10, 653). As tryptophan (*v. infra*) is also a constant constituent of protein it is not surprising that it is also degraded by bacterial action to indole. With some strains of bacteria ("indole negative") degradation only proceeds as far as indole-3-acetic acid and the positive Ehrlich reaction is only observed if "indole positive" bacilli are employed (*literature*: Sichel in Abderhalden, "Biochem. Handlexikon," Bd. XII, 1930, p. 234).

In addition to methods indicated above, indole may be obtained by extraction from coal tar (G.P. 223304, 454696) but is usually prepared by fusing phenylglycine *o*-carboxylic acid with caustic alkali at 280–290° (G.P. 85071) or at 250° under reduced pressure (G.P. 152548, 260327).

Indole forms leaflets, m.p. 52°, b.p. 253–254°, which are volatile in steam. In addition to chemical transformations indicated above, indole may be directly oxidised to indoxyl by activated oxygen and eventually to indigo (G.P. 130629).

In view of the occurrence of indole in body fluids a large number of qualitative tests for it have been proposed (*literature*: Hoppe-Seyler and Thierfelder, "Handb. d. physiol.- und patholog.-chem. Analyse," 9th ed., 1924, pp. 307, 936; Oppenheimer, "Handb. d. Biochem. d. Menschen u. Tiere," 1924, Vol. I, p. 255; Abderhalden, "Handb. d. biol. Arbeitsmethoden," Abt. I, Teil 4, 1923, p. 831; Teil 7, p. 783). Tosatti (Biochim. Terap. sperim. 1935, 22, 286) states that the Ehrlich reaction with *p*-dimethylaminobenzaldehyde, which Happold

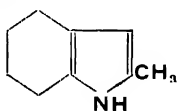


and Hoyle (Biochem. J. 1934, **28**, 1171) have used in the colorimetric assay of indole, surpasses all other known reactions and will detect 1 part in 5,000,000.

Pure indole may be titrated with iodine (Pauly and Gundermann, Ber. 1908, **41**, 4007), but there would seem to be no methods for its exact determination in mixtures. Larger quantities are estimated approximately as the picrate (Hesse, Ber. 1899, **32**, 2612); smaller amounts, e.g. in bacterial cultures, are distilled in steam and estimated colorimetrically by the nitrite method (Moraczewski, Z. physiol. Chem. 1908, **55**, 45), by naphthaquinonesulphonic acid (Herter and Foster, J. Biol. Chem. 1906, **1**, 257; Bergeim, *ibid.* 1917, **32**, 17), or by Ehrlich's reagent (*p*-dimethylaminobenzaldehyde) (Fellers and Clough, J. Bact. 1925, **10**, 105).

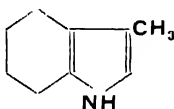
Indole has little direct application but is used in compounding artificial perfumes (G.P. 139822, 139869). Its presence in jasmine is said to be the prime reason for adding jasmine to tea, and indeed its detection in aromatic teas has been claimed as an indication of quality (Wang, Ni and Chen, J. Chem. Eng. China, 1937, **4**, 218).

### 2-Methylindole



is obtained from acetone phenylhydrazone (G.P. 238138; Fischer, "Anleitung zur Darst. org. Präparate," 1922, p. 68), or from aniline and chloroacetone (G.P. 40889). It forms needles, m.p. 59°, b.p. 272°. Like indole it is suitable for use as a perfume base (G.P. 139869), for the production of azo colours (G.P. 141351, 160674, 163141) and of medicinal arsenicals by direct reaction with arsenic acid (G.P. 240793).

### 3-Methylindole, skatole,

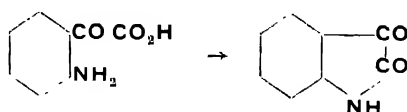


which accompanies indole in nature, may be separated by its non-reactivity towards 1:2-naphthaquinone-4-sulphonic acid (Herter and Foster, J. Biol. Chem. 1906, **2**, 267). Skatole forms leaflets, m.p. 95°, b.p. 285°. It gives a purple or violet-red coloration with vanillin in concentrated hydrochloric acid (Blumenthal, Biochem. Z. 1909, **19**, 527) which unlike that given by tryptophan is extracted by toluene (Kraus, J. Biol. Chem. 1925, **63**, 157) thus allowing a quantitative separation.

Hydroxy-derivatives of indole having hydroxyl groups in the pyrrole ring are of significance in that they are intermediates in almost all syntheses of indigo (*v.* INDOXYL COMPOUNDS).

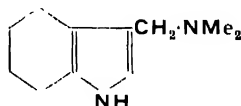
*Isatin*, 2,3-diketoidolone, behaves in many reactions as the lactam of isatinic acid, in which form it exists in alkaline solution; its formation by reducing 2-nitrophenyl-propionic, -glyoxylic and -pyruvic acids (Reissert, Ber.

1904, **37**, 1038) is then readily understood. It is obtained as sodium isatinate by allowing limited



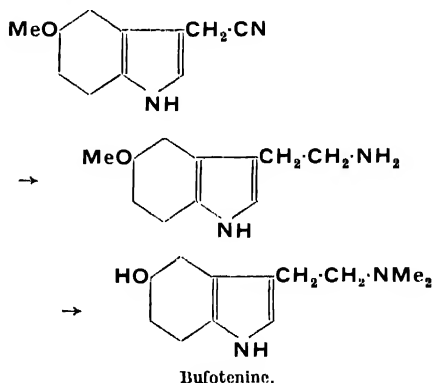
access of air during the fusion of phenylglycine with alkali (G.P. 105102) or preferably by the action of hot sulphuric acid on oximinoacetamide (Sandmeyer, Helv. Chim. Acta, 1919, **2**, 234; G.P. 320647; Organic Syntheses, Coll. Vol. 1, 321) or isatin-2-aml (G.P. 113979). Isatin forms orange-red prisms, m.p. 200-201°. In addition to its direct interest in connection with indigo, isatin has also been used in the production of thioindigoid colours (G.P. 182260; Bezdzik and Friedlaender, Monatsh. 1908, **29**, 376; *cf.* the colour reaction with thiophen in concentrated sulphuric acid with formation of indophenin) and other (*e.g.* halogenated) indigos.

*Gramine, donaxine (q.v.).*

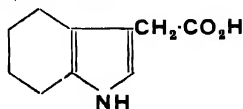


is an alkaloids directly derived from indole.

*Bufotenine*.—Of higher indoles bufotenine with a hydroxyl group in the aromatic ring is interesting as occurring in the secretion of the skin of toads (Wieland, Konz and Mittasch, Annalen, 1934, **513**, 1; Jensen and Chen, Ber. 1932, **65** [B], 1310). It was synthesised by reducing 5-methoxy-3-cyanomethylindole, methylating the resulting base and demethylating the phenolic methoxyl with aluminum chloride:



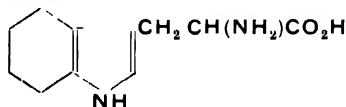
(*cf.* Hoshino and Shimodaira, Bull. Chem. Soc. Japan, 1936, **11**, 221; Annalen, 1935, **520**, 19).  
*β*-Indolyl-3-acetic acid.



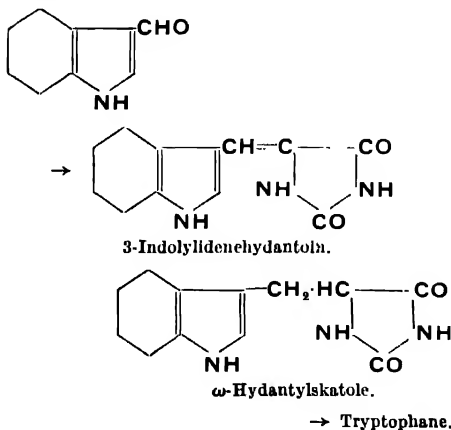
This acid has m.p. 164°, and is obtained by boiling the phenylhydrazone of  $\beta$ -formylpropionic phenylhydrazide with dilute alcoholic sulphuric acid and hydrolysing the product (Ellinger, Ber. 1904, **37**, 1806). It has for long been known to occur in normal and pathological urine, in the products of putrefaction of albumin, etc., and was for some time thought to be the chromogen in urine giving rise to "uroseoin," the red pigment formed in presence of nitrous acid (Ellinger and Flamand, Z. physiol. Chem. 1909, **62**, 285; cf. Ewins *et al.*, Biochem. J. 1913, **7**, 24; Homer, J. Biol. Chem. 1915, **22**, 353). A number of micro-organisms grown under controlled conditions were observed to elaborate a factor which influences cell elongation in the *Avena* coleoptile. This compound, *heteroauxin* was isolated by Kogl and his co-workers (Z. physiol. Chem. 1934, **228**, 113) and shown to be identical with indolyl-3-acetic acid from urine (*ibid.*, p. 104). v. AUXIN and GROWTH PROMOTERS.

A number of 5:7-di-iodoindole-3-acetic, -propionic acids and other iodinated indole and oxindole acids have been prepared by the Fischer hydrazone method and used as X-ray contrast media for therapeutic purposes (G.P. 425041, 459361, 436518; U.S.P. 1656239; Swiss P. 122243).

#### Tryptophan



is a constant constituent of protein, *e.g.* comprises 6–11% of the protein of human milk (Boccardo, *Pediatrics*, 1922, **30**, 257; see Abderhalden, "Biochem. Handlexikon, Bd. XII, p. 693). Its isolation by hydrolysing lactalbumin with baryta is described by Waterman (J. biol. Chem. 1923, **56**, 75), and it is conveniently synthesised by causing indole to react with ethyl magnesium iodide in anisole; the indole magnesium iodide is then converted into indole-3-aldehyde by formic ester and thence through 3-indolylidenehydantoin and  $\omega$ -hydantylskatole (Majuma and Kotake, Ber. 1922, **55**, 3859) to tryptophan:



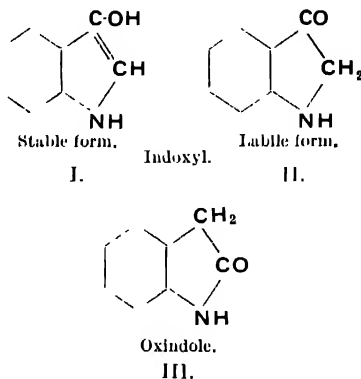
Racemic tryptophan has m.p. 289° and is slowly deaminated by acids with the formation of humin-like materials.

*Hypaphorine* is the betaine of tryptophan. (v. Vol. I, 686d).

A. H. C.

**INDOXYL COMPOUNDS.** *Indoxyl* is a nitrogenous organic compound of both industrial and biological importance; industrial, because it is an intermediate product in the technical synthesis of indigo; biological, because it occurs as a glucoside, *indican*, in indigo-yielding plants (see INDIGO, NATURAL), and also as a sulphuric ester in human urine.

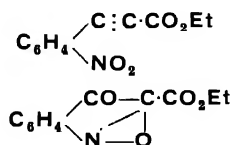
Chemically, indoxyl is 3-hydroxyindole, and is related to indole as  $\alpha$ -naphthol is to naphthalene. Indoxyl is a tautomeric substance, in that it behaves chemically as if it had both structures (I) and (II). The stable form is the phenolic form (I)



whilst the isomeric oxindole is stable in the ketonic form (III).

The plant glucoside indican has been fully discussed under INDIGO, NATURAL. The first observation that human urine deposited a blue colouring matter under certain conditions is attributed by Thudichum ("A Treatise on the Pathology of Urine," London, 1877) to Janus Plancus, 1767. The blue colouring matter was identified as indigo by Heller and Kletzinski, and Baumann (Pflügers Archiv, **13**, 291) with Brieger (Z. physiol. Chem. 1879, **3**, part 4) isolated the chromogen from urine and showed it to be the potassium salt of indoxyl sulphuric acid, decomposed by dilute acids into indoxyl and sulphuric acid (Baumann and Tiemann, Ber. 1880, **13**, 415).

Indoxyl was first synthesised by Baeyer (Ber. 1881, **14**, 1741) from ethyl *o*-nitrophenylpropionate, which with concentrated sulphuric acid undergoes rearrangement to ethyl isatogenate.



The latter by reduction yields ethyl indoxylate, hydrolysed by caustic soda to sodium in-



organic chemical reactions is that it limits, by the principle requiring the preservation of stable electron groups, the forms of electron displacement which it is permissible to assume in the interpretation of intramolecular electrical interaction. Two methods have been suggested by which electron duplets may undergo displacement with the preservation of the atomic octets and without alteration of the original arrangement of atomic nuclei. The first method is characterised by the circumstance that the displaced electrons remain bound in their original atomic octets; displacements of this type were postulated in 1923 by G. N. Lewis,<sup>1</sup> who showed how the electrostatic dissymmetry, arising from the unequal electron attraction of two different atoms linked together, could be propagated along a molecule by a mechanism analogous to electrostatic induction. This mode of electron displacement was considered to apply to a permanent molecular condition, therefore producing a permanent polarisation of the normal molecule: it has been called the *inductive effect*.<sup>2</sup> It is commonly represented by the use of arrow-headed bond signs indicating the direction towards which the electrons are concentrated:



Complementary to this mode of electron displacement is that which is characterised by the substitution of one electron duplet for another in the same atomic octet. This source of polarisation of the normal molecule is called the *mesomeric effect*.<sup>3</sup> The two effects form the main pillars of the theory of the polarisation of normal molecules, which has direct application in the interpretation of the physical properties (dipole moment, magnetic susceptibility, refractivity, nuclear and electronic spectra) of organic molecules, and the thermodynamics (heats and equilibria) of organic reactions. The same theory requires only to be supplemented by a closely analogous theory of polarisation accompanying activation in order to deal with the kinetics (activation heats and rates) of organic reactions.

In the theory of the polarisation of normal molecules, and, in particular, in that part of the theory which deals with the inductive effect, electron repulsion and attraction are regarded as relative phenomena: by convention the standard of reference is hydrogen. A group X would be described as repelling electrons if in  $\text{X}-\text{CR}_3$  the electron densities in the residue  $\text{CR}_3$  are greater than in  $\text{H}-\text{CR}_3$ . Similarly Y is said to be electron-attracting if in  $\text{Y}-\text{CR}_3$  the electron densities in  $\text{CR}_3$  are reduced by comparison with  $\text{H}-\text{CR}_3$ . Electron repulsions are conventionally distinguished by positive signs and attractions by negative signs, so that the inductive effects illustrated may be represented briefly by the symbols  $+I$  and  $-I$ :



It is inherent in the idea of intramolecular electrical interaction that the inductive effect exerted by groups must be influenced to some

extent by molecular environment, and although this effect is usually insufficient to change the qualitative behaviour of a substituent, it is convenient when commencing the task of classifying atoms and groups to set up the problem in a form in which the disturbance mentioned is minimal. This will be true if the groups considered are imagined to be singly present as substituents in a paraffin framework.

A major distinction must be drawn between charged and neutral groups. Anionic groups,

e.g.  $\text{O}^- \rightarrow$ ,  $\ddot{\text{S}}^- \rightarrow$ , as a whole are expected to repel electrons in comparison with neutral groups considered as a whole; and similarly cationic

groups, e.g.  $\text{R}_3\text{N}^+ \leftarrow$ ,  $\text{R}_3\text{S}^+ \leftarrow$ , as a class should attract electrons relatively to neutral groups as a class. The reason is that in anionic centres the atomic nuclei are over-compensated, and in cationic centres they are under-compensated, by the electrons of their own octets. Groups consisting of, or containing, formal dipolar ions, e.g.  $\rightarrow \ddot{\text{N}}\text{O}_2^+ \leftarrow$ ,  $\rightarrow \text{SOR}^+ \leftarrow$ ,  $\rightarrow \text{NC}^+ \leftarrow$ , should attract electrons relatively to neutral groups, since the former are invariably joined through their cationic centres to the remainder of the molecule. The electron-attracting effect of such a formal dipole should obviously be less than that of the corresponding free positive pole. It should be emphasised that these are general relationships, and that they take no account of the individual variations which may lead to occasional overlapping between the various series.

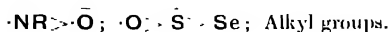
Individual distinctions depending on chemical type become apparent on considering a series of neutral groups. In the series  $\cdot\text{CH}_3$ ,  $\cdot\text{NH}_2$ ,  $\cdot\text{OH}$ ,  $\cdot\text{F}$ , the total nuclear and electronic charges are the same, but the distributed (protonic) portion of the nuclear charge in  $\cdot\text{CH}_3$  becomes progressively centralised in  $\cdot\text{NH}_2$ ,  $\cdot\text{OH}$ ,  $\cdot\text{F}$ , which therefore attract electrons from an attached atom successively more strongly in comparison with the methyl group (the polarity of alkyl groups is considered below). Again an atomic field is expected to suffer more loss through internal electronic deformation in larger than in smaller atoms, and thus inductive electron attraction should diminish along the series  $\cdot\text{F}$ ,  $\cdot\text{Cl}$ ,  $\cdot\text{Br}$ ,  $\cdot\text{I}$ . A regular connection between the inductive effect and position in the periodic table of the elements is indicated in this reasoning, and if R is a non-polar or feebly polar group (H, Alkyl), then all groups such as  $\cdot\text{NR}_2$ ,  $\cdot\text{OR}$ ,  $\cdot\text{SR}$ ,  $\cdot\text{Hal}$ ,  $\cdot\text{NR}$ ,  $\cdot\text{O}$ ,  $\cdot\text{N}$ , should attract electrons relatively to the methyl group. The extent of the attraction should increase with the number of the periodic group and decrease with increasing number of the period; it should also be greater in multiply-linked atoms than in the corresponding singly-linked atoms.

It can be deduced from the premises stated that the polarity of all alkyl groups is zero. This conclusion is, however, a formal one, directly connected with the choice of the paraffin framework as a means of standardising the effect of molecular environment. A more significant conclusion concerning alkyl groups is that, unlike the groups already considered (the intrinsic

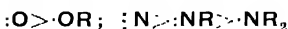
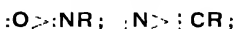
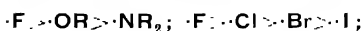
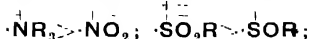
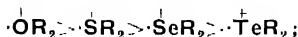
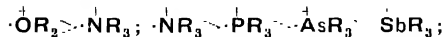
polarity of which renders their classification at least qualitatively insensitive to the disturbance of molecular environment), alkyl groups will essentially exert those polar effects which are impressed upon them by the other groups present in the molecule. In this connection the important property of alkyl groups is that they are much more polarisable than hydrogen, and thus  $\text{CH}_3$ , although it has no polarity in  $\text{CH}_3\text{—CH}_3$ , becomes an electron-repelling group in  $\text{CH}_3 \rightarrow \text{CO}_2\text{H}$ , and, in particular, it becomes so when comparison is made between  $\text{CH}_3 \rightarrow \text{CO}_2\text{H}$  and  $\text{H—C}$  the majority of substituents commonly encountered in organic molecules are attractors of electrons, alkyl groups generally function as weak electron-repelling groups. They do this also in hydrocarbon structures such as toluene, though the cause in this case is more appropriately classified with the mesomeric effect.

The conclusions reached in the preceding discussion are assembled for convenience in a table, in which the "greater than" sign,  $>$ , is used to indicate inequality of magnitude of the inductive effect:

*Electron Repulsion (+ I):*



*Electron Attraction (- I):—*



REFERENCES.

1. G. N. Lewis, "Valence and the Structure of Atoms and Molecules," (Chemical Catalogue Co., 1923, p. 139).
2. C. K. Ingold, Chem. Soc. Annual Rep. 1926, **23**, 129.
3. C. K. Ingold and E. H. Ingold, J.C.S. 1926, 1310; cf. C. K. Ingold, *ibid.* 1933, 1120.

C. K. I.

INDULINE SCARLET (Vol. I, 575d).

**INDULINES.** (Colour Index Nos. 859–863.) Dale and Caro (B.P. 1863 and Coupier in 1867) observed that on heating aminoazobenzene hydrochloride with aniline and its hydrochloride dark blue colouring matters were formed to which the name *Indulines* was given; these are insoluble in water but dissolve in alcohol (*Spirit-soluble Indulines*), whilst the free bases are soluble in oils and fats. Sulphonation yields water-soluble acid dyes known under a large variety of names such as *Fast Blue*, *Solid Blue*, *Cotton Blue*, etc.

The first induline was prepared empirically by Dale and Caro (B.P. 3307, 1863) by heating aniline hydrochloride with sodium nitrite, but it was soon appreciated that aminoazobenzene was an intermediate product and that by varying the conditions of formation different products could be obtained. The initial product is the so-called Azophenene (diaminoquinone dianil) which forms dark red crystals melting at  $240^\circ\text{C}$ ., and on further heating yields successively Induline B, 3B and finally 6B. On heating the spirit-soluble indulines first formed with aromatic bases other blue dyes of greater value are formed; thus with *p*-phenylenediamine the water-soluble *Paraphenylen Blue* is formed and with *p*-toluylenediamine water-soluble *Toluylen Blue* is obtained.

Such water-soluble indulines may also be prepared by a modification of the induline melt by allowing aminoazobenzene, aniline and aniline hydrochloride to react together in concentrated aqueous solution, or by heating azobenzene with aniline hydrochloride, *p*-phenylenediamine and a little ammonium chloride. Indulines are also formed as by-products in other processes such as the oxidation of crude aniline in the magenta melt.

Alternative methods of preparation are (a) from phenols or quinones and aminoazo-compounds, (b) from hydroxyazo-compounds and aniline, (c) from azobenzene and aniline hydrochloride at  $200\text{--}230^\circ\text{C}$ ., (d) by the action of *p*-diamines upon azo dyes derived from naphthylenediamines, (e) by melting aminoazobenzene or pre-formed indulines with benzidine hydrochloride to produce substantive cotton dyes.

By the addition of nitrobenzene or nitrophenols to the melt greyish-blue *Nigrosines* are produced; following the suggestion of Caro the name Induline is now reserved for those colouring matters produced from amines and azo-compounds whilst the name Nigrosine is reserved for those produced from nitrobenzene or nitrophenols.

On a large scale the dyes are prepared by heating the required base dissolved in aniline together with aniline hydrochloride (the "Induline melt"), the apparatus required consisting essentially of an enamelled still with oil heating, and provided with a suitable stirrer and condenser. Some details of the process may be found in Fierz-David, "Kunstliche Organische Farbstoffe" (1926), pp. 333–334.

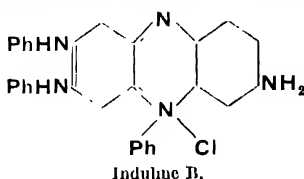
The uses of the spirit-soluble indulines are mainly confined to the preparation of spirit lacquers and varnishes whilst the free bases are used for colouring candles, waxes, etc. For textile purposes some use is made of the indulines for cotton printing, the colour dissolved in acetin being known as *Acetin Blue*, *Printing Blue*, etc., and in spite of the competition of newer and faster dyes the indulines still retain some measure of importance since the dyeings on silk and cotton on a tannin mordant are fairly fast.

The constitution of the dyes formed in the induline melt remained long in doubt, but the researches of O. Fischer and Hepp (Annalen, 1893, **272**, 306; 1895, **286**, 187) and in particular the classical investigations of F. Kehrman and

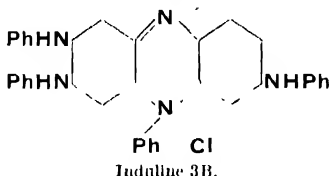
his pupils (*cf.* Kehrman and Klopfenstein, Ber. 1923, 56 [B], 2394) have now solved the problem.

The essential components of the melt have been shown to consist of various anilinophenyl-phenosafranines:

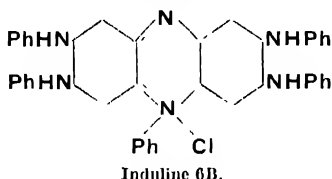
*Anilinophenyl-phenosafranine*,  $C_{30}H_{24}N_6Cl$ ,



*Anilinodiphenyl-phenosafranine*,  $C_{36}H_{28}N_6Cl$ ,

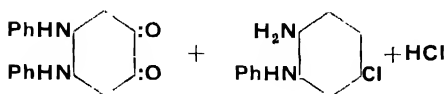


*Dianilinodiphenyl-phenosafranine*,  $C_{42}H_{33}N_6Cl$ ,

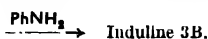


It is of course difficult to carry out the melt in such a manner as to obtain homogeneous products and the commercial dyestuffs are therefore mixtures of the above substances in varying proportions.

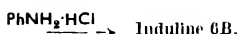
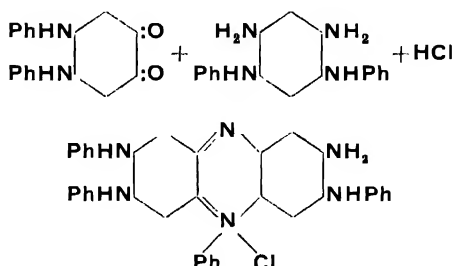
The proof of the accepted constitutional formula has been given by Kehrman (Helv. Chim. Acta, 1924, 7, 471; 1925, 8, 661; Ber. 1923, 56 [B], 2394), who by boiling 3-chloro-7-anilino-6-phenyl-*aposafranine* (from dianilino-*o*-quinone and 2-amino-5-chlorodiphenylamine hydrochloride) with aniline obtained 7-anilino-3:6-diphenyl-phenosafranine, which is identical with Induline 3B,



3-chloro-7-anilino-6-phenyl-*aposafranine*.

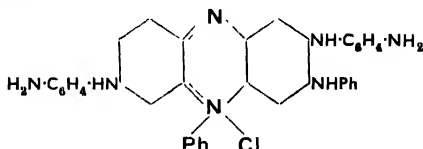


Using dianilino-*o*-quinone and *sym*-dianilino-*m*-phenylenediamine the product is 2-amino-7-anilino-3:6-diphenyl-phenosafranine which on heating with aniline and aniline hydrochloride yields Induline 6B:



Induline 6B is also formed on heating Induline 3B with aniline, aniline hydrochloride and mercuric oxide.

The water-soluble dyes such as Paraphenylene Blue probably have amino-groups attached to the side nuclei:



which would account for their solubility and increased basicity.

F. A. M.

**INDURITE** (Vol. IV, 465b).

**INFUSORIAL EARTH** (Vol. III, 579a).

**INHIBITORS, ANTIOXIDANTS.** Although isolated examples of the effect of small amounts of compounds in retarding the onset of atmospheric oxidation had been known for over a hundred years, this subject did not attain scientific or technical significance until 1917-18 with the work of Moureu and Dufraisse on the cause and prevention of the polymerisation of acrolein. They showed that the polymerisation was due to chemical reaction with the oxygen of the air and that both oxidation and polymerisation could be markedly delayed by traces of compounds termed by them "antioxygènes" which were themselves sensitive to atmospheric oxidation (Moureu and Dufraisse, Compt. rend. 1922, 174, 258).

It has now been fully established that auto-oxidisable substances of the most diverse type, both inorganic and organic, can be protected by a small amount of a reactive extraneous substance. These protective substances do not belong to any one class, but include elements such as iodine, salts such as sulphides and sulphites, derivatives of the non-metals and metal-oids, and a wide variety of organic compounds, particularly phenols and aromatic amines (Moureu and Dufraisse, Chem. Rev. 1926, 3, 113). Indeed, Dufraisse goes so far as to say

that every chemically reactive substance should be capable, under suitable experimental conditions, of functioning as an antioxidant.

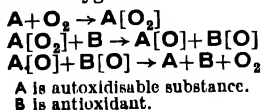
The technique used by the French workers in their researches was simple, and is still the basis of most methods of detecting antioxidant action. The autoxidisable substance is confined in an atmosphere of air or oxygen under suitable experimental conditions, and the rate of oxygen absorption measured manometrically in the presence and absence of the compounds being tested as antioxidants.

Antioxidant action is an example of negative catalysis, the antioxidant not only prolonging the induction period before oxidation becomes noticeable and rapid, but also reducing the steady oxidation rate which is attained in some oxidising systems. Even minute amounts of the catalyst may be effective, 1 part in a million of hydroquinone being sufficient to improve the stability of benzaldehyde to air.

Although antioxidants have been used to protect inorganic compounds such as sodium sulphite, their chief industrial outlet is in the preservation of organic compounds. Their first technical use was for the protection of vulcanised rubber, and this is still their biggest field. They are also used in petrol (*v. INHIBITORS, GUM*), mineral oils such as transformer and lubricating oils, fatty oils and waxes, aldehydes, etc. Anti-knocks for fuels function by an antioxidant mechanism, and the growing realisation of the significance of antioxidants in biological phenomena may be mentioned.

In practice, antioxidants are used at concentrations varying from 0.001% (petrol, aldehydes, etc.) to 1-2% (rubber) by weight on the autoxidisable substance. Technical antioxidants are usually organic compounds, the most widely used being aromatic compounds with a free phenolic group or a basic nitrogen atom. Among the phenols may be mentioned  $\beta$ -naphthol, catechol, hydroquinone and pyrogallol. Bases include *N*-phenyl- $\alpha$ - and  $\beta$ -naphthylamine (Du Pont, B.P. 276968); *NN'*-diphenyl-*p*-phenylenediamine (Goodyear, B.P. 305195); condensation products of aniline with acetone and of  $\alpha$ -naphthylamine with acetaldehyde, and substituted amines such as *pp'*-dimethoxydiphenylamine and *p*-benzylaminophenol.

It has been stated above that antioxidants are reactive substances which are themselves sensitive to oxygen. An antioxidant for one system may act as a pro-oxidant for another system, and even a change in concentration may change an antioxidant into a pro-oxidant. The first explanation of their action was the antagonistic oxide theory put forward by Moureu and Dufraisse in 1923 (*Compt. rend.* 1923, 176, 624). On this theory, the first reaction is the formation of an unstable peroxide of the autoxidisable substance; this reacts with the antioxidant to give two unstable oxides, which decompose to regenerate the original substance, the antioxidant and molecular oxygen.



This theory is not now generally accepted. The present view is that autoxidation proceeds by a chain mechanism, the unstable peroxide first formed initiating reaction chains throughout the autoxidisable substance. The antioxidant functions by reacting with the unstable peroxide to give deactivated products, thus breaking the chain-propagating mechanism (*see, for example, Christiansen, Trans. Faraday Soc.* 1928, 24, 714). Each time a chain is broken, an antioxidant molecule is destroyed. This mechanism has been shown to hold for the autoxidation of substances as varied as benzaldehyde (Bäckström and Beatty *J. Physical Chem.* 1931, 35, 2530) and rubber (Morgan and Naunton, *Proc. Rubber Tech. Conf., London*, 1938, p. 599).

**R. F. G.**  
**INHIBITORS, GUM.** The term "gum-inhibitors" has been applied to numerous organic compounds that have the power of preventing the formation of resinous or gum-like material in motor spirits during storage. Gum<sup>1</sup> formation in motor spirits is a liquid-phase oxidation process and gum-inhibitors are a special class of antioxidants (*v. INHIBITORS, ANTI-OXIDANTS*).

Attention was drawn to the formation of gum in motor spirits as a result of the development, since about 1910, of the cracking process for the conversion of gas oil and other high-boiling fractions of petroleum into motor spirit. The petrol produced, particularly by vapour-phase cracking processes, was found to be highly unstable, readily formed gum, and darkened in colour on storage. Its use in internal-combustion engines caused the choking of jets, and the formation of resinous deposits in the induction manifold and inlet-valve pockets, and on the inlet-valve stems, causing them to stick in the guides with consequent loss of engine power and erratic running. These objectionable properties were considered to be due to the high proportion of unsaturated hydrocarbons (olefins) present in this type of petrol. Although these disadvantages could be largely overcome by drastic refining treatment with sulphuric acid or other reagents, this was costly owing to the considerable losses of material, as well as the expense for plant, labour and reagents.

The subsequent demand for motor fuels of increasing anti-knock value further emphasised the importance of this problem, since it was found that the highly unstable petrols produced by vapour-phase cracking processes had a high anti-knock value, but this was reduced to a considerable extent by the refining treatment necessary to render them sufficiently stable.

A somewhat similar position arose in connection with the increasing use of benzole as an anti-knock blending agent in petrols after the 1914-18 war. The crude benzole produced at coke ovens and gas works contains up to 10% or more of unsaturated hydrocarbons, and unless these constituents are removed almost completely, the benzole is liable to cause troubles due to gum when used in engines.

Attention was first drawn to an alternative

<sup>1</sup> The terms "gum" and "resin" have been used in this article synonymously and in a purely descriptive

and much more satisfactory method of treatment for fuels of this type by the publication in 1930 of the investigations on gum formation of the Research Committee of The National Benzole Association (Great Britain). These investigations showed (1) that engine troubles due to the use of unstable fuels are caused almost entirely by non-volatile gum already present in the fuel at the time of use (Rept. of of Research Committee, Nat. Benzole Assoc. 1926, p. 97; V. Voorhees and J. O. Elvinger, *J. Soc. Automotive Eng.* 1929, **24**, 584; E. B. Humm, H. G. M. Fischer and A. J. Blackwood, *ibid.* 1930, **26**, 31; S. P. Marley and W. A. Gruse, *Ind. Eng. Chem.* 1932, **24**, 1298), and (2) that the deterioration and gumming of the fuel prior to its use in an engine can be prevented by the addition of very small quantities of certain substances, such as phenols and aromatic amines. These conclusions were supported by large-scale storage tests and fleet trials (Repts. of Research Committee, Nat. Benzole Assoc. 1927-30; W. H. Hoffer and G. Claxton, *Fuel*, 1930, **9**, 359, 440, 476).

The use of such substances enabled the drastic refining treatment hitherto found necessary to be considerably reduced or almost entirely eliminated, thus not only effecting considerable economies in the expense of reagents, etc., but also avoiding the destruction of material having valuable anti-knock properties. These advantages have led to the wide use of gum-inhibitors in connection with the production of cracked petrols, benzoles and other motor fuels containing unsaturated hydrocarbons.

#### General Nature of the Gumming Process.

—When motor fuels containing unsaturated hydrocarbons are stored, the non-volatile material, known as gum, is produced at a rate depending both on the nature of the fuel and the conditions of storage. There is often a preliminary period when the rate of gum formation is small, followed by the production of gum at an increasing rate. At first the gum remains dissolved in the fuel, but when the saturation limit, which varies considerably with different fuels, has been reached, the gum separates out.

The gumming process is accompanied by a marked fall in the anti-knock properties of the fuel. E. W. J. Mardles and H. Moss (*J. Inst. Petroleum Tech.* 1929, **15**, 657; *see also* J. C. Morrell, C. D. Lowry, C. G. Dryer and G. Egloff, *Ind. Eng. Chem.* 1934, **26**, 497) have attributed this to (1) fouling of the interior of the engine, (2) the presence of peroxides (*see below*) which are strong knock-inducers, and (3) the partial removal of hydrocarbons of high anti-knock value. Gum formation is also often associated with an increase in colour, although this is by no means a definite indication of gumming. Thus, extensive gum formation occurs in some motor fuels without any noticeable deterioration of colour, whereas with other fuels increase in colour occurs with practically no increase in gum content (B. T. Brooks, *ibid.* 1926, **18**, 1198; Rept. of Research Committee, Nat. Benzole Assoc. 1926, p. 41).

It has now been definitely established that gum formation does not occur in the absence of air, and it is generally agreed that it is primarily

an air-oxidation process, i.e. the polymerisation reactions giving rise to the formation of gum are initiated by oxidation.

As early as 1918, B. T. Brooks and I. Humphrey (*J. Amer. Chem. Soc.* 1918, **40**, 822) suggested that the diolefins rather than the mono-olefins were the chief cause of gum formation. B. T. Brooks, "The Non-Benzenoid Hydrocarbons," New York, 1922, p. 427, also drew a parallel between the oxidation of pinene and of unsaturated petroleum oils, and advanced the view that the first step in the production of gum from cracked petrols is the formation of peroxides of the diolefins, which break up with the formation of aldehydes, ketones, water and carbon dioxide, and yield organic acids on further oxidation. The pale yellow fluid gum formed from cracked petrols on exposure to air consists mainly of organic peroxides, aldehydes and ketones, whilst the resin that remains after prolonged evaporation consists largely of resin acids. N. A. C. Smith and M. B. Cooke (*U.S. Bur. Mines Rept. Invest.* 1922, No. 2394) similarly concluded that (1) gums are caused by oxidation, but have no relationship to the unsaturation as determined by sulphuric acid absorption, and (2) gums are polymerised aldehydes formed by olefin oxidation.

That diolefins which readily form peroxides are mainly, although not entirely, responsible, has been confirmed by D. T. Flood, J. W. Hladky and A. Edgar (*Oil Gas J.* 1930, **29**, No. 18, 40; *Ind. Eng. Chem.* 1933, **25**, 1234) and by H. A. Cassar (*ibid.* 1931, **23**, 1132; *see also* P. N. Kogerman, *Trans. Second World Power Conf.* (Berlin), 1930, **8**, 33), who have compared the relative stabilities of various pure unsaturated hydrocarbons, and by S. M. Martin, Jr., W. A. Gruse and A. Lowry (*Ind. Eng. Chem.* 1933, **25**, 381) who found that when diolefins were removed from cracked petrols by maleic anhydride, by sulphuric acid or by partial hydrogenation, gum was no longer formed.

The connection between peroxides and gum formation has since been emphasised by L. G. Story, R. W. Provine and H. T. Bennett (*ibid.* 1929, **21**, 1079) J. A. C. Yule and C. P. Wilson (*ibid.* 1931, **23**, 1254), E. W. J. Mardles and H. Moss (*loc. cit.*), G. Egloff and his co-workers (*ibid.* 1934, **26**, 497, 655, 885; 1936, **28**, 465), and other investigators. Peroxides can be detected at a very early stage of oxidation at which no aldehyde or acid and practically no gum is to be found. The rate of formation of peroxides accelerates with time. Gum is formed in considerable amounts as soon as much peroxide is present, and before the formation of any appreciable amounts of aldehydes or acids, which appear therefore to be secondary reaction products. According to Yule and Wilson there is a relation between the gum content and "peroxide number" of cracked petrols.

Although the general character of the gumming process is now well established and there is strong evidence that the first step is the formation of organic peroxides, the mechanism of the further reactions finally leading to the formation of gum is still obscure. Since the general nature of the process is one of oxidation, it is to be expected that under normal storage-conditions gumming



will depend on the accessibility of air to the fuel. It is also influenced by a number of other factors, such as temperature, actinic light, material of the containing vessel, and the presence of substances which may either promote or retard the reactions involved.

**Action of Gum-Inhibitors.**—Any peroxides and gum already present in a raw motor spirit are removed during fractional distillation, which is usually an essential feature of any refining process. Thereafter, formation of peroxide and gum may recommence immediately or, as already stated, there may be a short delay or "induction period" before gumming commences. The effect of adding an inhibitor is to cause a very prolonged induction period before oxidation commences, apparently by preventing the initial formation of peroxides as postulated by C. Moureu and C. Dufraisse (Chem. Rev. 1926, 3, 113) for antioxidants in general. During this period the further reactions leading to the formation of gums, to darkening in colour and to fall in anti-knock value are suppressed. A very wide range of organic compounds has been found to be capable of prolonging the induction period, some being much more effective than others. The most efficient are those containing a phenolic group, and the property appears to be possessed to the greatest degree by substances that are themselves readily oxidised.

Gum-inhibitors do not prevent gum formation indefinitely, they only delay the commencement of the process. However, since efficient gum-inhibitors in suitable concentrations, which may vary from one-thousandth to a few hundredths of 1%, are capable of prolonging the induction period under normal storage-conditions for many months, or years, this is not of any practical consequence.

**Gum Tests.**—In connection with the study and application of inhibitors, it is necessary to consider the tests available for determining the quantity of gum in a fuel at any particular time, *i.e.* the so-called *preformed or existent gum*, and those used for determining the tendency of a fuel to form gum on further storage, *i.e.* the so-called *potential gum*. Clearly, the relative tendency of fuels to form gum can be determined by storing them for a definite period and then determining the existent gum. Such storage tests, however, take too long to be of practical use, and it has been found necessary to devise much more rapid laboratory tests.

(i) **Determination of Existent Gum.**—Numerous tests have been suggested for this purpose, all of them involving evaporation of the fuel under defined conditions and measurement of the non-volatile residue. The chief difficulty has been to prevent further oxidation and gumming of the fuel during evaporation. Clearly, the method of evaporation that gives the lowest result will approximate most closely to the true gum content of the fuel.

The earliest tests consisted of merely allowing the fuel to evaporate from a glass or copper dish heated on a boiling-water bath (100°C.). Sometimes the gum obtained in this way was subsequently "dried" by further heating at a higher temperature. It was found, however, that further gumming occurred during the tests,

particularly with fuels containing high-boiling constituents. Moreover, with certain fuels the copper apparently catalysed the formation of gum (*see below*). N. A. C. Smith and M. B. Cooke (U.S. Bur. Mines Rept. Invest. 1922, No. 2394; M. B. Cooke, *ibid.* 1925, No. 2686) proposed a steam-bath method and porcelain dishes to eliminate these effects. Attempts were also made to simulate engine-manifold conditions by subjecting the fuel to flash evaporation (W. S. Norris and F. B. Thole, J. Inst. Petroleum Tech. 1929, 15, 681), or passing the vaporised air-fuel mixture over a hot plate (E. B. Hunn, H. G. M. Fischer and A. J. Blackwood, J. Soc. Automotive Eng. 1930, 26, 31). Methods involving vacuum distillation were also tried (W. Littlejohn, W. H. Thomas and H. B. Thompson, J. Inst. Petroleum Tech. 1930, 16, 684; and O. C. Bridgeman and E. W. Aldrich, J. Soc. Automotive Eng. 1931, 28, 191). All these methods have now been superseded by "air-jet tests." These have been developed from a procedure originally proposed by Hunn, Fischer and Blackwood, which consisted in allowing a stream of air to impinge on the surface of the fuel during evaporation on a water bath. Under these conditions the fuel evaporates much more rapidly and further oxidation is almost entirely eliminated, no perceptible differences being observed when the air is replaced by nitrogen or carbon dioxide. Various modifications of the original method, in which higher temperatures are employed and the air is preheated, have been suggested (M. J. Mulligan, W. G. Lovell and T. A. Boyd, Ind. Eng. Chem. [Anal.], 1932, 4, 351). A conventional air-jet test has now been adopted tentatively as a standard by the Institute of Petroleum in Great Britain ("Standard Methods of Testing Petroleum and its products," 1935, p. 206) and a more elaborate method employing a hot air-jet, by the American Society for Testing Materials in the U.S.A. ("A.S.T.M. Standards on Petroleum Products and Lubricants," 1939, p. 150).

(ii) **Determination of Potential Gum.**—Numerous tests have similarly been devised for determining potential gum. Practically all of them, although differing in the conditions used, depend on the same principle, *viz.*, intensifying the conditions of oxidation. In some of the tests, the gum formed during a definite period of oxidation is measured, in others the length of the induction period, as indicated by oxygen absorption.

The earliest test, which was first developed as a test for corrosion, involved evaporating the fuel from a polished copper dish. The copper was considered to catalyse the formation of gum. Subsequently, further work cast considerable doubt on the significance of the results, since they were often at variance with those of engine and storage tests (Rept. of Research Committee, Nat. Benzole Assoc. 1926, pp. 41 *et seq.*; V. Voorhees and J. O. Eisinger, J. Soc. Automotive Eng. 1929, 24, 584; and E. B. Hunn, H. G. M. Fischer and A. J. Blackwood, *l.c.*).

A test which has been standardised internationally for benzoles (W. H. Hoffer and G. Claxton, Gas J. 1932, 200, 494; Nat. Benzole

Assoc. "Standard Specifications for Benzole and Allied Products," 1938, p. 109) consists in bubbling oxygen through the fuel whilst it is heated at 100°C. in a flask with reflux condenser, the gum formed during a definite period being finally determined. This test, however, is unsuitable for highly volatile fuels owing to loss of fuel in the oxygen stream. For petrols, a better procedure, and one which is particularly suitable for the study of inhibitors, is that originally proposed by V. Voorhees and J. O. Eisinger (J. Soc. Automotive Eng. 1929, 24, 584) and recommended by T. H. Rogers, J. L. Bussies and P. T. Ward (Ind. Eng. Chem 1933, 25, 397). It consists of heating the fuel with oxygen in a flask in a steam bath (fig. 1) and observing the

rate at which oxygen is absorbed, by means of a manometer connected to the flask. In this way the induction period is measured or, if desired, the gum content of the fuel may also be determined after a definite period of oxidation. Numerous tests have also been devised in which the fuel is heated under pressure with oxygen in a metal bomb (E. B. Hunn, H. G. M. Fischer and A. J. Blackwood, *l.c.*; E. W. Aldrich and N. P. Robie, J. Soc. Automotive Eng. 1932, 30, 198; O. C. Bridgeman, Oil Gas J. 1932, 31, No. 3, 55; G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer, Ind. Eng. Chem. 1932, 24, 1375; J. W. Ramsay, *ibid.* 1932, 24, 539; B. P. Ward, Oil Gas J. 1932, 31, No. 12, 16; C. Winning and R. M. Thomas, Ind. Eng. Chem.

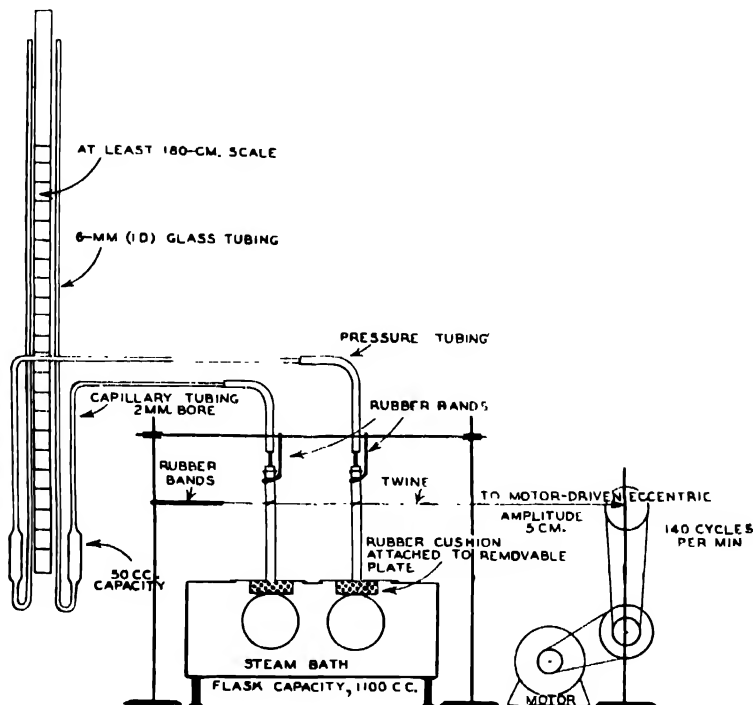


FIG. 1.

1933, 25, 511; W. H. Thomas, Proc. World Petroleum Congr. 1933, 2, 122), the size of bomb, material, quantity of fuel and technique, however, varying considerably.

The standard test adopted tentatively by the Institute of Petroleum in Great Britain consists in heating the fuel with air in a flask immersed in a steam bath for a definite time, and subsequently determining the existent gum ("Standard Methods for Testing Petroleum and its Products," 1935, p. 208). The A.S.T.M. have standardised tentatively a metal bomb test, in which the induction period is measured, as in the Voorhees and Eisinger test, by a recording manometer ("A.S.T.M. Standards on Petroleum Products and Lubricants," Committee D.2, 1939, p. 153).

Correlation of these tests with actual storage tests has proved extremely difficult, and only a rough relationship has been established (W. H. Hoffert and G. Claxton, *l.c.*; T. H. Rogers, J. L. Bussies and P. T. Ward, *l.c.*; C. G. Dryer, J. C. Morrell, G. Egloff and C. D. Lowry, Ind. Eng. Chem., 1935, 27, 15; "A.S.T.M. Standards on Petroleum Products and Lubricants," Committee D.2, 1939, p. 9). Hence it is advisable to check any conclusions drawn from them by actual storage tests. Moreover, owing to the fact that it is impossible to cover in a single test the many storage conditions used in practice, it is desirable to allow a high factor of safety with regard to the stability requirements of motor fuels.

A further limitation with regard to potential

gum tests has been pointed out by E. W. J. Mardles (Proc. World Petroleum Congr. 1933, 2, 57, 116). At the high temperature used (100°C.) the relative efficiencies of inhibitors may differ considerably from their relative efficiencies under normal storage-conditions. A substance may even exhibit practically no inhibiting effect under the conditions of a potential gum test, although quite effective at atmospheric temperatures. An example of this is afforded by hydroquinone, which has little or no inhibiting effect under the conditions of a bomb test (G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer, Ind. Eng. Chem. 1932, 24, 1375), but is quite effective under normal storage-conditions. For this reason Mardles prefers incubation tests on samples of the fuel at 35°C. to oxidation tests at 100°C. However, most of the substances that give rise to these anomalies have only feeble inhibiting power, and no examples appear to have been reported in which the converse occurs, the substance having a much lower inhibiting effect than that indicated by potential gum tests.

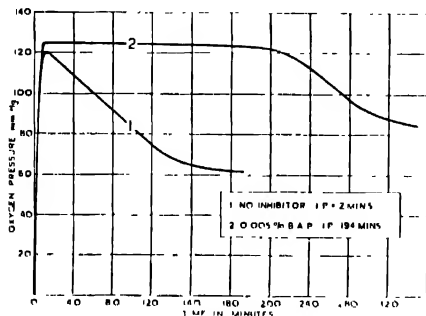


FIG. 2.

#### Effect of Concentration of Inhibitor.—

As already mentioned, the effect of adding an inhibitor to a motor fuel containing unsaturated hydrocarbons is to cause an induction period before gum is formed on storage or under the conditions of potential gum tests. Typical results are shown in figs. 2 and 3.

With an efficient inhibitor in low concentration in a moderately unstable fuel, the increase in the induction period, as indicated by oxygen absorption, is directly proportional to the concentration of inhibitor. Typical results due to T. H. Rogers and V. Voorhees (*ibid.* 1933, 25, 520) are given in fig. 4. With very unstable fuels, however, or when high concentrations of inhibitors of low efficiency are used, considerable deviations from this simple relationship are found (Du Pont de Nemours & Co., "Gasoline Antioxidants," Tech. Bull. No. 4). Thus, when the induction period is plotted against the inhibitor concentration, a curve is obtained which may become horizontal. In other words, further addition of inhibitor gives no increase in induction beyond this point, and it may be entirely impossible to obtain a satisfactory induction period.

If the induction period is measured with respect

to gum, it is often found that a small amount of gum is formed during the induction period, either from the fuel itself or from the inhibitor, by secondary reactions. Moreover, the inhibitor may be non-volatile, thus increasing the residue left on evaporation (W. H. Hoffert and G.

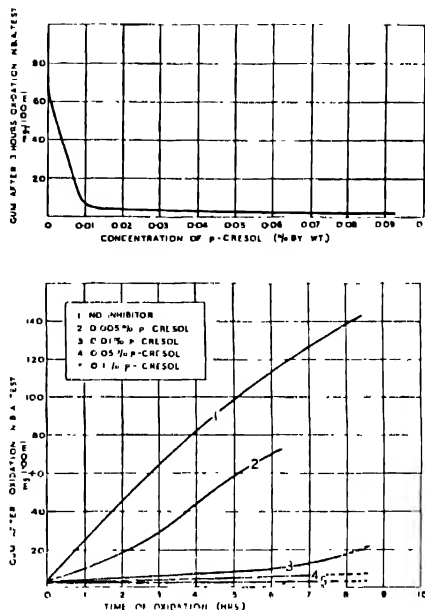


FIG. 3.

Claxton, J.S.C.I. 1933, 52, 25T). Hence the problem of determining the amount of inhibitor to use in practice resolves itself into either (1) a potential gum test to determine the quantity of inhibitor that will give a required induction period, e.g. 400 minutes by the Voorhees and Eisinger test, which is claimed to be equivalent

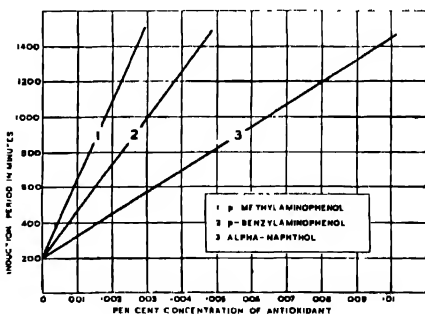


FIG. 4.

to a storage life of about 1 year under temperate climatic conditions, or (2) determination of the concentration of inhibitor that will reduce to, e.g. 10 mg. per 100 ml., the quantity of gum formed during a definite time of oxidation in a potential gum test. When either of these

Assoc. "Standard Specifications for Benzole and Allied Products," 1938, p. 109) consists in bubbling oxygen through the fuel whilst it is heated at 100°C. in a flask with reflux condenser, the gum formed during a definite period being finally determined. This test, however, is unsuitable for highly volatile fuels owing to loss of fuel in the oxygen stream. For petrols, a better procedure, and one which is particularly suitable for the study of inhibitors, is that originally proposed by V. Voorhees and J. O. Eisinger (J. Soc. Automotive Eng. 1929, **24**, 584) and recommended by T. H. Rogers, J. L. Bussies and P. T. Ward (Ind. Eng. Chem. 1933, **25**, 397). It consists of heating the fuel with oxygen in a flask in a steam bath (fig. 1) and observing the

rate at which oxygen is absorbed, by means of a manometer connected to the flask. In this way the induction period is measured or, if desired, the gum content of the fuel may also be determined after a definite period of oxidation. Numerous tests have also been devised in which the fuel is heated under pressure with oxygen in a metal bomb (E. B. Hunn, H. G. M. Fischer and A. J. Blackwood, *l.c.*; E. W. Aldrich and N. P. Robie, J. Soc. Automotive Eng. 1932, **30**, 198; O. C. Bridgeman, Oil Gas J. 1932, **31**, No. 3, 55; G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer, Ind. Eng. Chem. 1932, **24**, 1375; J. W. Ramsay, *ibid.* 1932, **24**, 539; B. P. Ward, Oil Gas J. 1932, **31**, No. 12, 16; C. Winning and R. M. Thomas, Ind. Eng. Chem.

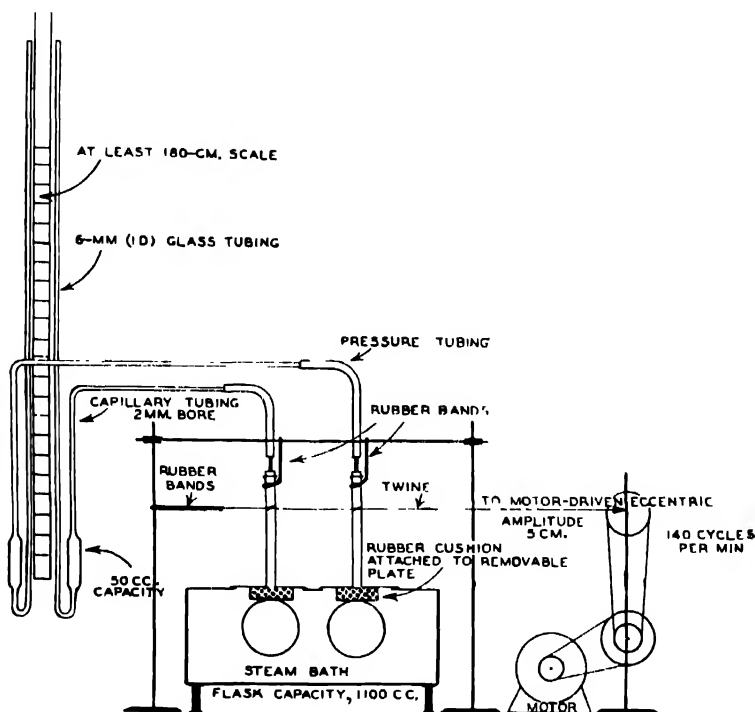


FIG. 1.

1933, **25**, 511; W. H. Thomas, Proc. World Petroleum Congr. 1933, **2**, 122), the size of bomb, material, quantity of fuel and technique, however, varying considerably.

The standard test adopted tentatively by the Institute of Petroleum in Great Britain consists in heating the fuel with air in a flask immersed in a steam bath for a definite time, and subsequently determining the existent gum ("Standard Methods for Testing Petroleum and its Products," 1935, p. 208). The A.S.T.M. have standardised tentatively a metal bomb test, in which the induction period is measured, as in the Voorhees and Eisinger test, by a recording manometer ("A.S.T.M. Standards on Petroleum Products and Lubricants," Committee D.2, 1939, p. 153).

Correlation of these tests with actual storage tests has proved extremely difficult, and only a rough relationship has been established (W. H. Hoffert and G. Claxton, *l.c.*; T. H. Rogers, J. L. Bussies and P. T. Ward, *l.c.*; C. G. Dryer, J. C. Morrell, G. Egloff and C. D. Lowry, Ind. Eng. Chem., 1935, **27**, 15; "A.S.T.M. Standards on Petroleum Products and Lubricants," Committee D.2, 1939, p. 9). Hence it is advisable to check any conclusions drawn from them by actual storage tests. Moreover, owing to the fact that it is impossible to cover in a single test the many storage conditions used in practice, it is desirable to allow a high factor of safety with regard to the stability requirements of motor fuels.

A further limitation with regard to potential

gum tests has been pointed out by E. W. J. Mardles (Proc. World Petroleum Congr. 1933, 2, 57, 116). At the high temperature used (100°C.) the relative efficiencies of inhibitors may differ considerably from their relative efficiencies under normal storage-conditions. A substance may even exhibit practically no inhibiting effect under the conditions of a potential gum test, although quite effective at atmospheric temperatures. An example of this is afforded by hydroquinone, which has little or no inhibiting effect under the conditions of a bomb test (G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer, Ind. Eng. Chem. 1932, 24, 1375), but is quite effective under normal storage-conditions. For this reason Mardles prefers incubation tests on samples of the fuel at 35°C. to oxidation tests at 100°C. However, most of the substances that give rise to these anomalies have only feeble inhibiting power, and no examples appear to have been reported in which the converse occurs, the substance having a much lower inhibiting effect than that indicated by potential gum tests.

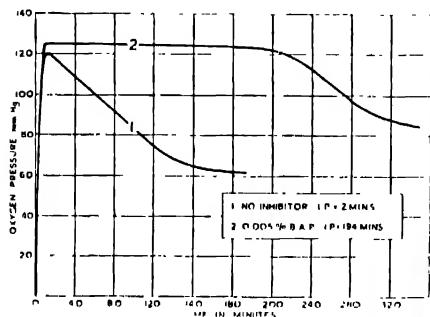


FIG. 2.

**Effect of Concentration of Inhibitor.**—As already mentioned, the effect of adding an inhibitor to a motor fuel containing unsaturated hydrocarbons is to cause an induction period before gum is formed on storage or under the conditions of potential gum tests. Typical results are shown in figs. 2 and 3.

With an efficient inhibitor in low concentration in a moderately unstable fuel, the increase in the induction period, as indicated by oxygen absorption, is directly proportional to the concentration of inhibitor. Typical results due to T. H. Rogers and V. Voorhees (*ibid.* 1933, 25, 520) are given in fig. 4. With very unstable fuels, however, or when high concentrations of inhibitors of low efficiency are used, considerable deviations from this simple relationship are found (Du Pont de Nemours & Co., "Gasoline Antioxidants," Tech. Bull. No. 4). Thus, when the induction period is plotted against the inhibitor concentration, a curve is obtained which may become horizontal. In other words, further addition of inhibitor gives no increase in induction beyond this point, and it may be entirely impossible to obtain a satisfactory induction period.

If the induction period is measured with respect

to gum, it is often found that a small amount of gum is formed during the induction period, either from the fuel itself or from the inhibitor, by secondary reactions. Moreover, the inhibitor may be non-volatile, thus increasing the residue left on evaporation (W. H. Hoffert and G.

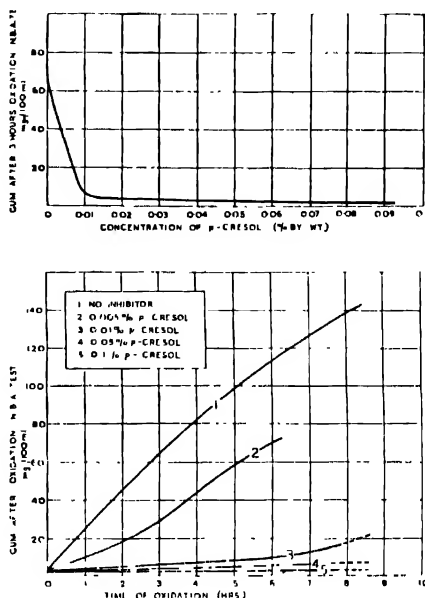


FIG. 3.

(Clayton, J.S.C.I. 1933, 52, 25T). Hence the problem of determining the amount of inhibitor to use in practice resolves itself into either (1) a potential gum test to determine the quantity of inhibitor that will give a required induction period, e.g. 400 minutes by the Voorhees and Eisner test, which is claimed to be equivalent

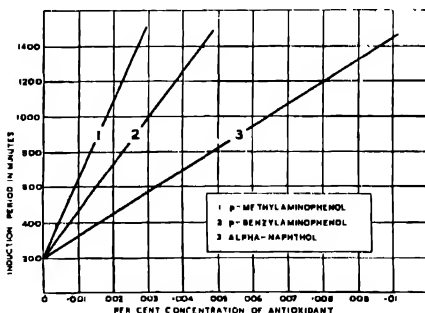


FIG. 4.

to a storage life of about 1 year under temperate climatic conditions, or (2) determination of the concentration of inhibitor that will reduce to, e.g. 10 mg. per 100 ml., the quantity of gum formed during a definite time of oxidation in a potential gum test. When either of these

methods is applied, it is found that the concentration of inhibitor required varies considerably according to the particular substance used, and also according to the character of the fuel to which it is added.

**Relation of Chemical Composition and Inhibiting Power.**—Data concerning the relative inhibiting efficiencies of various organic compounds have been published by G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer (*i.e.*: Proc. World Petroleum Congr. 1933, **2**, 50, *see also* G. Egloff, W. F. Faragher and J. C. Morrell, *Refiner*, 1930, **9**, No. 1, 80), T. H. Rogers and V. Voorhees (*Ind. Eng. Chem.* 1933, **25**, 520; *Oil Gas J.* 1933, **32**, No. 11, 13; Proc. World Petroleum Congr. 1933, **2**, 63) and other investigators. The method usually adopted has been to compare the increase in the induction period, determined with respect to oxygen absorption, when the same concentration of the various compounds has been added to different portions of the same fuel. Unfortunately, the actual concentrations of the added substances, the types of fuel and the conditions of oxidation used by different investigators have varied considerably. Moreover, owing to the fact that the relationship between concentration and the induction period may not be linear, it is not always safe to reduce the results to the same concentration of the added substance.

Some observers have merely compared the quantities of gum obtained with a single concentration of the various substances after a fixed time of oxidation. Since the relative quantities of gum will differ considerably, depending on whether this time is longer or shorter than the induction period, such results give little or no indication of relative inhibiting power.

Further difficulties have arisen owing to the instability of the base fuels and to differences in the stability of distillates from the same stock of raw material, since T. H. Rogers and V. Voorhees (*Oil Gas J.* 1933, **32**, No. 11, 13) have shown that the relative effectiveness of inhibitors depends to a certain extent on the initial stability of the fuel used. Thus it is not surprising that widely different relative efficiencies have been reported, and that there is disagreement as to whether certain substances have any inhibiting effect. However, certain conclusions can be drawn as to the types of compounds that are most effective, and a number of generalisations have been brought to light with regard to the effects of the introduction of substituent groups into different classes of organic compounds. The effect of substitution is important not only because it indicates the direction in which improvement in inhibiting efficiency may be made, but also because it influences the solubility relationships of inhibitors with regard to motor fuels and water, which are important under practical conditions (*see below*).

There is general agreement that phenols and aminophenols are by far the most effective classes of organic compounds. Certain aromatic amines have high inhibiting efficiencies. On the other hand, aliphatic alcohols and aliphatic amines have little or no inhibiting effect.

(i) **Phenols.**—Data on phenolic compounds are given in table I—A. It will be noted that

phenol has only moderate inhibiting action under the conditions used. The inhibiting property of the hydroxyl group, however, is intensified by the introduction of alkyl groups into the ortho- or para-positions, whereas these have little or no effect when introduced into the meta-position. Thus, the *ortho*- and *para*-cresols are considerably more effective than phenol, whilst *meta*-cresol has only about the same efficiency. Two alkyl groups are considerably more effective than a single group. Again they are most effective when they are in the ortho- and para-positions to the hydroxyl group. This superiority of an ortho- or para-substituted compound over the meta-compound has also been encountered in a number of other series. On the other hand, the substitution of the hydrogen in the hydroxyl group by an alkyl group, *e.g.* anisole and phenetole, causes entire loss of inhibiting properties.

When additional hydroxyl groups are introduced into a phenol, the inhibiting action is increased. As with alkyl radicals, a hydroxyl group in the ortho- or para-position is much more effective than one in the meta-position. Catechol, for example, has powerful inhibiting properties, whereas resorcinol is only slightly more effective than phenol. Again, pyrogallol is one of the most powerful inhibitors known, whereas phloroglucinol, in which the hydroxyl groups are in the meta-position to one another, is far less effective.

The ethers of polyphenols have no inhibiting effect, but the presence of both an ether group and a hydroxyl group in the same molecule, *e.g.* eugenol and guaiacol, confers moderate inhibiting properties.

Among hydroxynaphthalene compounds,  $\alpha$ -naphthol is very effective, whilst the  $\beta$ -compound is much less so. This difference may be compared with the effects of ortho- and meta-substitution in the phenols. 1:5-Dihydroxynaphthalene is a powerful inhibitor.

In general the introduction of a nitro-group into a phenol decreases inhibiting efficiency, as illustrated by the fact that nitrophenol is less effective than phenol. The introduction of a nitroso group, however, increases the effect, *p*-nitrosophenol being a highly effective inhibitor.

(ii) **Amines.**—As a class, the aromatic amines are not so effective as the phenols or aminophenols (table I—B). Aniline and the toluidines have only feeble inhibiting action. The diamines and secondary amines, however, are considerably more powerful.  $\alpha$ -Naphthylamine has moderate inhibiting properties, but the  $\beta$ -compound is much less effective, a relationship similar to that exhibited by the naphthols.

(iii) **Aminophenols.**—An amino-group in any position in a compound containing a phenolic hydroxyl group increases inhibiting power, the effect again being usually most marked when the amino-group is in the ortho- or para-position (table I—C). The replacement of one of the amino-hydrogens also results in a considerable increase in inhibiting efficiency, but when both hydrogens of the amino-group are replaced, as in *p*-benzalamino-phenol, the activity falls off considerably. This substitution in the amino group has also been used to increase the solubility of aminophenols in motor fuels,

TABLE I.—INCREASE IN INDUCTION PERIOD (MIN.) CAUSED BY ADDITION OF 0.01% OF VARIOUS SUBSTANCES.

Reference.	(G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer <sup>1</sup> )	(T. H. Rogers and V. Voorhees <sup>2</sup> )*	(W. H. Hoffert, G. Claxton and E. G. Hancock <sup>3</sup> )
Test.	U O P Bomb test	Voorhees and Eisinger test.	Voorhees and Eisinger test.
Fuel.	Pennsylvania cracked petrol (induction period 45 minutes).	Cracked petrol (induction period varied and given in brackets).	Benzole (induction period 0 minutes).
<b>A—AROMATIC HYDROXY-COMPOUNDS</b>			
<i>Monohydroxy-</i>			
Phenol . . . . .	30	3 (55)	20
<i>o</i> -Cresol . . . . .	90	9 (55)	100
<i>m</i> -Cresol . . . . .	30	—	—
<i>p</i> -Cresol . . . . .	165	9 (55)	—
Tricresol (tech.) . . . . .	90	—	—
Butylphenol ( <i>o</i> - and <i>p</i> -) . . . . .	150	—	—
<i>tert</i> -Butylphenol ( <i>o</i> - and <i>p</i> -) . . . . .	165	—	—
Butylcresol . . . . .	—	40 (230)	—
4-Hydroxy-1:3-dimethylbenzene . . . . .	375	—	—
2-Hydroxy-1:3-dimethylbenzene . . . . .	375	—	150
5-Hydroxy-1:3-dimethylbenzene . . . . .	—	—	20
4-Hydroxy-1:2-dimethylbenzene . . . . .	210	—	—
2-Hydroxy-1:4-dimethylbenzene . . . . .	240	—	—
<i>o</i> -Benzylphenol . . . . .	—	—	30
<i>p</i> -Benzylphenol . . . . .	—	—	30
<i>p</i> -Phenylphenol . . . . .	—	95 (335)	—
<i>p cyclo</i> Hexylphenol . . . . .	—	10 (230)	—
3-Methyl-4-benzylphenol . . . . .	—	—	30
4-Methyl-2-benzylphenol . . . . .	—	—	110
Thymol . . . . .	255	—	—
Carvacrol . . . . .	135	—	—
2-Hydroxydiphenyl . . . . .	15	—	< 20
3-Hydroxydiphenyl . . . . .	90	—	< 20
<i>p</i> -Nitrosophenol . . . . .	—	690 (90)	—
<i>Polyhydroxy-</i>			
Catechol . . . . .	2,355	—	2,050
Resorcinol . . . . .	105	—	—
Orcinol . . . . .	105	—	—
Hydroquinone . . . . .	40	75 (55)	210
4-Butylresorcinol . . . . .	315	—	—
4-Hexylresorcinol . . . . .	345	170 (230)	—
4-Heptylresorcinol . . . . .	255	—	—
Toluidhydroquinone . . . . .	25	—	—
Pyrogallol . . . . .	2,140	975 (90)	6,800
Phloroglucinol . . . . .	45	—	—
3-Methylcatechol . . . . .	—	—	3,400
Butylcatechol . . . . .	—	—	3,000
Benzylcatechol (mixed isomers) . . . . .	—	—	1,550
4:4'-Dihydroxydiphenyl . . . . .	—	500 (335)	500
<i>Mono- and di-hydroxycyclic-</i>			
$\alpha$ -Naphthol . . . . .	2,205	—	710
$\beta$ -Naphthol . . . . .	285	15 (55)	—
1:5-Dihydroxynaphthalene . . . . .	1,660	120 (135)	1,250
1:4-Dihydroxyanthraquinone . . . . .	—	—	< 20
1:5-Dihydroxyanthraquinone . . . . .	—	—	< 20
Nitroso- $\beta$ -naphthol . . . . .	90	—	—
Wood tar phenols . . . . .	—	110 (115)	260

<sup>1</sup> Ind. Eng. Chem. 1932, **24**, 1375; Proc. World Petroleum Congr. 1933, **2**, 50.<sup>2</sup> Ind. Eng. Chem. 1933, **25**, 520; Oil Gas J. 1933, **32**, No. 11, 13; Proc. World Petroleum Congr. 1933, **2**, 63.<sup>3</sup> Int. Conf. Benzole Producers, 1930, and unpublished results.

\* Results at 0.01% of added substance calculated assuming linear relationship between induction period and concentration.

TABLE I.—INCREASE IN INDUCTION PERIOD (MIN.) CAUSED BY ADDITION OF 0.01% OF VARIOUS SUBSTANCES—*continued*.

Reference	(G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer <sup>1</sup> ).	(T. H. Rogers and V. Voorhees <sup>2</sup> ). <sup>a</sup>	(W. H. Hoffert, G. Claxton and E. G. Hancock <sup>3</sup> ). <sup>a</sup>
Test	U. O. P. Bomb test.	Voorhees and Eisinger test.	Voorhees and Eisinger test.
Fuel	Pennsylvania cracked petrol (induction period 45 minutes)	Cracked petrol (induction period varied and given in brackets).	Benzole (induction period 0 minutes)
<b>B—AROMATIC AMINES</b>			
<i>Mono-amines</i>			
Aniline . . . . .	0	2 (55)	—
<i>o</i> -Toluidine . . . . .	15	—	—
<i>m</i> -Toluidine . . . . .	15	—	—
<i>p</i> -Toluidine . . . . .	15	—	—
Xylidine . . . . .	0	—	—
Dimethylaniline . . . . .	0	—	—
Ethyl- <i>o</i> -toluidine . . . . .	0	—	—
<i>o</i> -Nitro-aniline . . . . .	0	—	—
Diphenylamine . . . . .	60	20 (55)	—
4-Aminodiphenyl . . . . .	0	—	20
<i>Polyamines</i>			
<i>o</i> -Phenylenediamine . . . . .	405	—	—
<i>m</i> -Phenylenediamine . . . . .	120	50 (55)	—
<i>p</i> -Phenylenediamine . . . . .	915	385 (55)	810
<i>m</i> -Toluylenediamine . . . . .	195	—	—
<i>p</i> -Aminodimethylaniline . . . . .	590	—	—
<i>p</i> -Aminodichethylaniline . . . . .	330	—	—
<i>pp'</i> -Diaminodiphenylamine . . . . .	900	—	—
Benzidine . . . . .	150	6 (55)	—
<i>o</i> -Tolidine . . . . .	75	—	—
2,4-Diaminodiphenylamine . . . . .	835	—	—
Dibutylbenzidine . . . . .	—	135 (90)	—
<i>p</i> -Aminodiphenylamine . . . . .	—	—	2,250
<i>Naphthylamines</i>			
$\alpha$ -Naphthylamine . . . . .	60	17 (55)	—
$\beta$ -Naphthylamine . . . . .	30	—	—
Ethyl- $\alpha$ -naphthylamine . . . . .	120	—	—
Phenyl- $\alpha$ -naphthylamine . . . . .	675	—	—
Phenyl- $\beta$ -naphthylamine . . . . .	150	—	—
<b>C—AMINOPHENOLS</b>			
<i>o</i> -Aminophenol . . . . .	1,275	450 (55)	—
<i>m</i> -Aminophenol . . . . .	285	—	—
<i>p</i> -Aminophenol . . . . .	2,295	430 (55)	—
2,4-Diaminophenol . . . . .	—	800 (90)	—
2-Amino-5-hydroxytoluene . . . . .	1,740	—	—
2-Amino-4-nitrophenol . . . . .	1,215	—	—
<i>p</i> -Methylaminophenol . . . . .	—	1,745 (55)	—
<i>p</i> -Benzylaminophenol ("B.A.P.") . . . . .	—	1,100 (120)	2,800
<i>p</i> -Phenylaminophenol . . . . .	—	860 (120)	—
<i>p</i> -Benzalaminophenol . . . . .	—	200 (80)	—
Cinnamal- <i>p</i> -aminophenol . . . . .	—	150 (80)	—
1-Hydroxy-2:6-dimethyl-4-aminobenzene . . . . .	—	—	7,720
<i>p</i> -Dibenzylaminophenol (di "B.A.P.") . . . . .	—	—	1,820
4-Amino-4'-hydroxydiphenyl . . . . .	—	—	100
4-Amino- $\beta$ -naphthol . . . . .	—	350 (135)	—

<sup>1</sup> Ind. Eng. Chem. 1932, 24, 1375; Proc. World Petroleum Congr. 1933, 2, 50.<sup>2</sup> Ind. Eng. Chem. 1933, 25, 520; Oil Gas J. 1933, 32, No. 11, 13; Proc. World Petroleum Congr. 1933, 2, 63.<sup>3</sup> Int. Conf. Benzole Producers, 1936, and unpublished results.<sup>a</sup> Results at 0.01% of added substance calculated assuming linear relationship between induction period and concentration.



TABLE I.—INCREASE IN INDUCTION PERIOD (MIN.) CAUSED BY ADDITION OF 0.01% OF VARIOUS SUBSTANCES—*continued*.

Reference.	(G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer <sup>1</sup> ).	(T. H. Rogers and V. Voorhees <sup>2</sup> ). <sup>*</sup>	(W. H. Hoffert, G. Claxton and E. G. Hancock <sup>3</sup> ). <sup>*</sup>
Test.	U.O.P. Bomb test.	Voorhees and Elisinger test.	Voorhees and Elisinger test.
Fuel.	Pennsylvania cracked petrol (induction period 45 minutes)	Cracked petrol (induction period varied and given in brackets).	Benzole (induction period 0 minutes).
<b>D—MISCELLANEOUS COMPOUNDS</b>			
Anthracene . . . . .	0	0 (125)	—
Phenanthrene . . . . .	0	0 (125)	—
Urea . . . . .	0	2.5 (60)	—
Furfuramide . . . . .	—	40 (90)	—
Aldol- $\alpha$ -naphthylamine . . . . .	—	40 (55)	—
Phenylhydrazine . . . . .	195	0 (55)	—
Benzalphenylhydrazine . . . . .	5	0 (90)	—
Cinnamalphenylhydrazine . . . . .	—	110 (90)	—
Hydrazobenzene . . . . .	0	2 (55)	—
<i>pp'</i> -Diaminohydrazobenzene . . . . .	—	420 (90)	—
<i>p</i> -Aminoazobenzene . . . . .	—	0 (90)	100
Diazoaminobenzene . . . . .	—	—	20
<i>p</i> -Hydroxyazobenzene . . . . .	—	0 (90)	—
Thiourea . . . . .	10	5 (60)	20
<i>p</i> -Thiocresol (0.05%) . . . . .	0	0 (90)	—
<i>o</i> -Thiodiphenylamine . . . . .	1,395	150 (135)	—
Nicotine . . . . .	0	0 (90)	—
Brucine . . . . .	—	0 (60)	—
8-Hydroxyquinoline . . . . .	—	—	120
<i>p</i> -Hydroxyphenylmorpholine . . . . .	—	—	1,240
Tributylamine . . . . .	0	—	120

<sup>1</sup> Ind. Eng. Chem. 1932, 24, 1375; Proc. World Petroleum Congr. 1933, 2, 50.<sup>2</sup> Ind. Eng. Chem. 1933, 25, 520; Oil Gas J. 1933, 32, No. 11, 13; Proc. World Petroleum Congr. 1933, 2, 63.<sup>3</sup> Int. Conf. Benzole Producers, 1936, and unpublished results.<sup>\*</sup> Results at 0.01% of added substance calculated assuming linear relationship between induction period and concentration.

*p*-benzylaminophenol being one of the best inhibitors so far discovered.

(iv) *Compounds of Other Types*.—Table I—D gives the results for a miscellaneous group of compounds, some of them of interest owing to patent claims for inhibiting properties. Aromatic nitro-compounds have only slight action. Chloro-compounds are ineffective, but the introduction of a chlorine atom into an inhibitor molecule makes little change in its effectiveness. 1:2-Naphthaquinone possesses inhibiting effect, but 1:4-naphthaquinone and other quinones and ketones have little or no effect. Of a number of nitrogen compounds, mostly cyclic, studied by Egloff, only phenylhydrazine and 8-hydroxyquinoline had inhibiting properties. Of the sulphur compounds thiodiphenylamine showed marked inhibiting power. The thiocresols, however, were ineffective. The alkaloids have been reported as antioxidants, but Rogers and Voorhees found that they had no effect. Of the hydrazines and hydrazobenzenes, only diaminohydrazobenzene was effective. Certain dyes, *e.g.* indophenol, are quite effective (C. D. Lowry, G. Egloff, J. C. Morrell and C. G. Dryer, Ind. Eng. Chem. 1935, 27, 413; C. L. Gutzeit

and Standard Oil Development Co., B.P. 385066; C. Winning, L. E. Sargent and J. F. Dudley and Standard Oil Development Co., B.P. 383511).

**Hydrocarbon Standard for Evaluating Inhibitors.**—Since the publication of the data on relative inhibiting efficiencies, given above, a method of overcoming difficulties caused by changes in the base fuel has been proposed by C. G. Dryer, C. D. Lowry, G. Egloff and J. C. Morrell (Ind. Eng. Chem. 1935, 27, 315), who have described a standardised method of rating the efficiencies in terms of *cyclohexene*, as a primary standard. The efficiency of an inhibitor is expressed as a "*cyclohexene number*," *i.e.* the number of minutes by which the induction period of *cyclohexene* is increased by the addition of 0.002% of the inhibitor. It may be calculated from tests on reference petrols (secondary standards), the relationship of which to *cyclohexene* has been determined by standardisation with  $\alpha$ -naphthol. Inhibitors with a low solubility in the standard petrols may be dissolved first in an organic solvent, *e.g.* benzene or hexane, that does not affect the induction period.

**Correlation of Inhibiting Action and Oxidation-Reduction Potential.**—C. D. Lowry, G. Egloff, J. C. Morrell and C. G. Dryer (*ibid.* 1933, **25**, 804) have drawn attention to the fact that the "critical oxidation potentials" of inhibiting substances can be correlated with their value as inhibitors, as determined by an accelerated oxidation test. The term "critical oxidation potential" introduced by L. F. Fieser (J. Amer. Chem. Soc. 1930, **52**, 5204), is the potential at which the rate of oxidation of the reductant of an oxidation-reduction system becomes so small as to be just detectable.

The correlation is shown in table II for a number of aromatic hydroxy-compounds selected to cover a wide potential range and tested in equimolecular concentrations in a cracked petrol. It will be noted that as the

TABLE II.—COMPOUNDS CONTAINING HYDROXYL GROUPS  
(0.00005 g.-mol. per 100 g. petrol.)

	Critical oxidation potential (volts) <sup>1</sup>	Induction period (minute)
Pennsylvania cracked gasoline alone . . . .		45
<i>p</i> -Nitrophenol . . . .	1.133	45
<i>o</i> -Nitrophenol . . . .	1.133	60
<i>m</i> -Nitrophenol . . . .	1.147	60
Phenol . . . .	1.089	60
<i>m</i> -Cresol . . . .	1.080	90
<i>o</i> -Cresol . . . .	1.040	120
<i>p</i> -Cresol . . . .	1.038	165
2-Hydroxy-1,4-dimethylbenzene . . . .	1.038 (Calc.)	
4-Hydroxy-1,2-dimethylbenzene . . . .	1.036 (Calc.)	150
<i>p</i> -Hydroxydiphenyl . . . .	1.036	150
$\beta$ -Naphthol . . . .	1.017	
2-Hydroxy-1,3-dimethylbenzene . . . .	0.895 (Calc.)	
4-Hydroxy-1,3-dimethylbenzene . . . .	0.895	
Phloroglucinol . . . .	0.799	1,920
$\alpha$ -Naphthol . . . .	0.797	1,890
Catechol . . . .	0.742	
1,5-Dihydroxynaphthalene . . . .	0.673	1,380
Hydroquinone . . . .	0.631	135
Pyrogallol . . . .	0.609	1,440

<sup>1</sup> Data from Fieser (J. Amer. Chem. Soc. 1930, **52**, 5204) except calculated values.

potential decreases, the induction period lengthens, shows a sharp peak between 0.800 and 0.700 volt, and drops slightly at still lower potentials. The variations in induction period with changes in structure, to which attention has already been drawn, are paralleled by similar relationships between oxidation potential and structure. Thus the superiority in inhibiting effect of ortho- or para-substituted compounds over their meta-isomers—shown by catechol over resorcinol or in the cresols and xylcnols—is accompanied by corresponding differences in oxidation potentials. Similarly, the superiority of  $\alpha$ - over  $\beta$ -naphthol is related to the lower potential of the former compound.

It will be noted that two of the compounds, phloroglucinol and hydroquinone, have shorter induction periods than would be expected from

their oxidation potentials. The weak inhibiting action of the former compound is possibly due to its existence in the ketonic form (C. Moureu and C. Dufraisse, *Compt. rend.* 1922, **174**, 258), whilst attention has already been drawn to the anomalous behaviour of hydroquinone in accelerated oxidation tests, this compound being a highly effective inhibitor at normal temperatures.

A similar relation between inhibiting action and critical oxidation potential was found with the amines. However, this relationship represents a general trend, rather than an absolute index of inhibiting value.

**Colour Stability.**—Certain inhibitors, as already mentioned, give rise to colour formation in motor fuels, particularly when exposed to light. This colour formation, which usually increases with the concentration of the inhibitor, is probably due to "parasitic" reactions whereby the inhibitor is gradually destroyed during the induction period. It has been found that certain substances termed "secondary stabilisers" exert a protective or colour-stabilising action on gum-inhibitors. The aliphatic amines, particularly the butyl- and amyl- amines appear to be the most effective (L. V.

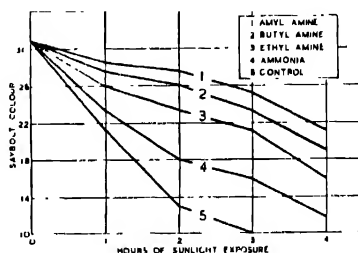


FIG. 5.

Sorg, *Ind. Eng. Chem.* 1935, **27**, 156), and have been used for preventing colour formation in certain types of cracked petrol stabilised with  $\alpha$ -naphthol or "B.A.P." (H. M. Steninger, *ibid.* 1934, **26**, 1039). The optimum amount varies from 0.002 to 0.004% by wt. regardless of the original colour of the petrol, larger quantities giving no additional improvement. The effect of substituent groups on the amines as colour stabilisers is shown in fig. 5.

According to J. B. Rather and L. C. Beard (*Oil Gas J.* 1936, **34**, No. 52, 209) the following inhibitors have been used for preserving the colour of cracked distillates and kerosenes: thiocarbamide, hydroquinone, resorcinol, catechol, pyrogallol, phloroglucinol, 1:2:4-trihydroxybenzene, butylpyrogallol, alkyl-substituted polyhydroxybenzenes, ethanolamines, urea and thiourea. Many of these compounds possess the additional property of decolorising cracked petrols and kerosenes that have gone off colour on storage. The usual procedure is to agitate the off-colour oil with a solution of the reagent in alcohol at the rate of 1 lb. of reagent to 2,000–15,000 gallons of oil, according to the initial colour.

**Requirements for Gum-Inhibitors.**—The various properties that have been stated to

govern the suitability or otherwise of a substance as a gum-inhibitor for motor fuels may be summarised as follows (P. G. Somerville and W. H. Hoffert, B.P. 289347, 1926; W. H. Hoffert and G. Claxton, Proc. World Petroleum Congr. 1933, 2, 69; T. H. Rogers and V. Voorhees, Ind. Eng. Chem. 1933, 25, 520; Oil Gas J. 1933, 32, No. 11, 13; C. G. Dryer, J. C. Morrell and G. Egloff, *ibid.* 1937, 35, No. 45, 113, 116):

- (1) It should possess a high efficiency for performing its primary purpose—the stabilisation of the fuel.
- (2) It should be soluble in the fuel at atmospheric temperatures to an appreciably greater extent than that required for effective stabilisation.
- (3) The quantity required, or its volatility, must be such that little or no residue is left when the fuel is evaporated.
- (4) It should be more soluble in the fuel than in water, so that it is not removed by any water the fuel may come into contact with during storage and distribution.
- (5) It should not of itself cause discoloration of the fuel and should inhibit discoloration in both light and dark storage.
- (6) It must not affect adversely the normal combustion of the fuel or lead to obnoxious combustion products.
- (7) It should not cause the fuel to have any corrosive properties.
- (8) It should not be unduly volatile nor possess any offensive odour, and should not be detrimental to the health of operators and workmen handling it.
- (9) It must be available in adequate commercial quantities at a reasonable cost.

Owing to the fact that motor fuels are often stored in contact with water, the solubility of inhibitors in water is an important factor. The differences in the ease with which certain inhibitors are removed by water is shown in table III, which gives the decrease in the induction period caused by shaking benzole containing 0.01% by wt. of various inhibitors with water (W. H. Hoffert, G. Claxton and E. G. Hancock, *unpublished Rept. Int. Conf. Benzole Producers*, 1936).

TABLE III.

Inhibitor.	Induction period, minutes per 0.01% of inhibitor	
	Before washing with water.	After washing with 4 vol water.
N-Benzyl- <i>p</i> -aminophenol	2,800	2,600
Catechol	2,050	60
N-Dibenzyl- <i>p</i> -aminophenol	1,820	1,560
1-5-Dihydroxynaphthalene	1,250	520
<i>p</i> -Hydroxyphenylmorpholine	1,240	210
$\alpha$ -Naphthol	730	730
Wood-tar distillate	260	150
1-Hydroxy-2,6-dimethylbenzene	150	150
<i>o</i> -Cresol	100	90

Owing to these stringent requirements, only a relatively few compounds have been used commercially.

For cracked petrols, catechol was one of the first to be tried, but was found to be too easily removed by water.  $\alpha$ -Naphthol was more satisfactory in this respect, but tended to cause discoloration. Both these inhibitors were replaced by mono- and *p*-dibenzylaminophenol (Antioxidants Ltd. and Standard Oil Co. (Indiana), B.P. 350438) and certain wood-tar acids (Universal Oil Products Co., C. D. Lowry and C. G. Dryer, B.P. 410115; *see also* U.O.P. Booklet No. 224, 1938). *iso*Propylmonomethyl-, monobutyl- and mono-isobutyl-derivatives of *p*-aminophenol have also been used recently (Kodak, Ltd., B.P. 503316, 503401). For benzoles and coal spirits, cresol (P. G. Somerville and W. H. Hoffert, B.P. 289347) has been used in Great Britain, as well as both cresol and catechol, whilst *p*-benzylaminophenol has been used in the U.S.A.

The following particulars with regard to *p*-benzylaminophenol ("B.A.P."), one of the best inhibitors so far developed, are of interest. It is produced commercially as an odourless, light-brown powder, melting between 84° and 90°C. The quantities normally required for stabilising motor fuels vary from 0.0005 to 0.005%. It is of high purity and less than 20% is insoluble in petrol or benzole. At 25°C. its solubility in anhydrous methanol is about 60%, and in 95% ethyl alcohol about 65%. It is soluble in water to about 0.06% at 25°C., whilst its solubility in petrols at this temperature varies from 0.1 to 0.5%, depending upon the nature of the petrol. It has a higher solubility in aromatic-type spirits and dissolves in motor benzole at 25°C. to the extent of about 1.35%. Hence its distribution coefficient between motor fuels and water ranges from 1.7 to 22.5. Provided it is not used in excessive quantity, it does not discolour motor fuels in the absence of alkali, and generally improves their colour stability.

The comparative effectiveness of "B.A.P." and a wood-tar distillate are illustrated by the following results (table IV), (V. Voorhees, Proc. World Petroleum Congr. 1933, 2, 63).

TABLE IV.

Fuel	Induction period (minutes).	Ratio of amounts of inhibitor required to give 400 minutes induction period.
<i>Low Stability Petrol</i>		
Unstabilised	115	21.1
"B.A.P." 0.001% . . .	285	
"B.A.P." 0.0025% . . .	660	
Wood-tar distillate 0.0025% . . .	120	
" " 0.01% . . .	225	
" " 0.05% . . .	600	
<i>Moderate Stability Petrol</i>		
Unstabilised	275	10:1
"B.A.P." 0.001% . . .	620	
" " 0.0025% . . .	930	
Wood-tar distillate 0.005% . . .	450	

**Influences of Material of Containing Vessel and Suppression of Metal Catalysts.**—Metals and metallic compounds have long been recognised as oxidation catalysts. In paints and varnishes, for example, oxides and soaps of metals, particularly those possessing multiple valence states, are used as driers (W. M. MacKay and H. Ingle, J.S.C.I. 1916, **35**, 454; 1917, **36**, 317; see also DRYING OILS, Vol. IV, p. 916). The autoxidation by metallic catalysts of unsaturated hydrocarbons (R. Willstätter and E. Sonnenfeld, Ber. 1913, **46**, 2952; R. Criegee, Annalen, 1930, **481**, 263), of petroleum hydrocarbons (C. R. Wagner and J. Hyman, J. Amer. Chem. Soc. 1930, **52**, 4345; 1931, **53**, 3019) and of phenols (W. Treibs, Brennstoff-Chem. 1933, **14**, 81) has also been studied. Hence some effect of the material of the containing vessel on gum formation is to be expected.

W. H. Hoffert and G. Claxton (Repts. Research Committee, Nat. Benzole Assoc. 1927, p. 128; 1928, p. 63; 1929, p. 58) have shown that, compared with glass, copper containers reduce the quantity of gum formed from benzoles when phenols are absent (fig. 6), but increase gum formation in their presence. Iron and tin also appeared to reduce gum formation in the absence of inhibitors. Similar results were obtained when these metals were introduced into the flask in the N.B.A.<sup>1</sup> oxidation test, or when gumming was promoted by the action of ultra-violet light. E. W. J. Mardles and A. Moss (J. Inst. Petroleum Tech. 1929, **15**, 657) have confirmed that copper and other metals can have an inhibiting effect on gum formation from cracked petrols during incubation tests at 35°C. Organo-metallic compounds have also been patented as inhibitors for preventing the oxidation of lubricating and transformer oils (H. L. Callendar, R. O. King and E. W. J. Mardles, B.P. 295230, 1927; W. Helmore and E. W. J. Mardles, B.P. 398222, 1932; E. A. Evans and C. C. Wakefield, B.P.

267174, 1925). These results indicate that the effect of metals on the gumming of motor fuels depends on whether certain constituents other than hydrocarbons are present. Metals have a deleterious effect on *inhibited* motor fuels, causing a decrease in induction period both on storage and during potential gum tests. The

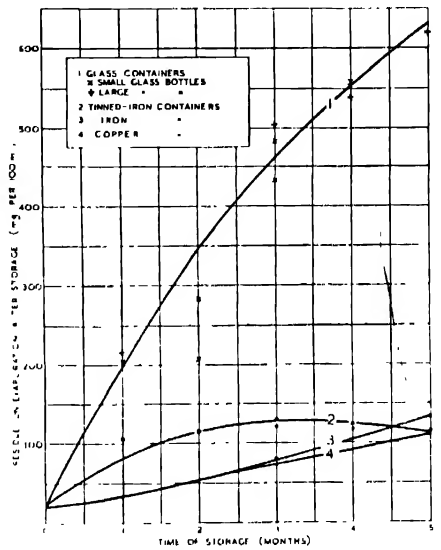


FIG. 6.

decrease of induction period of inhibited benzoles caused by introducing strips of various metals (6.5 sq. in.) into the flask in the Voorhees and Eismger potential gum test is shown in table V (W. H. Hoffert, G. Claxton and E. G. Hancock, unpublished Rept. Int. Conf. Benzole Producers, 1936).

Copper and rusty steel considerably reduced the length of the induction period with most of

<sup>1</sup> National Benzole Association.

TABLE V

Inhibitor.	Induction period (minute per 0.01%)						
	Glass	Zinc	Tin	Al	Clean steel	Rusty steel	Rust.
Pyrogallol . . . . .	6,800	1,380	—	—	1,170	80	—
"B.A.P." . . . . .	2,800	780	2,840	1,430	1,320	350	900
Catechol . . . . .	2,050	410	2,120	1,230	1,180	120	200
di-"B.A.P." . . . . .	1,820	800	—	—	—	470	—
p-Hydroxyphenylmorpholine . . . . .	1,250	350	1,320	1,190	1,000	560	1,300
1:5-Dihydroxynaphthalene . . . . .	1,240	280	—	—	—	260	—
p-Phenylenediamine . . . . .	810	220	660	590	570	70	400
α-Naphthol . . . . .	710	180	—	580	360	570	910
Wood-tar distillate . . . . .	260	60	360	250	120	70	90
1-Hydroxy-2:6-dimethylbenzene . . . . .	150	90	160	120	90	190	170
o-Cresol . . . . .	100	50	90	80	50	90	100

the inhibitors. Zinc, tin and aluminium had only a minor effect. In general, monohydric phenols were less affected than polyhydric phenols and amines. The effect of rust is important, because most inhibited motor fuels are stored in mild steel or wrought-iron vessels. Hydrated ferric hydroxide appeared to be the reactive component. In the tests with copper and steel, copper and iron could be detected in solution in the benzole at the end of the induction period. The metal probably reacts with the inhibitor, thus reducing the quantity available. Similar results were obtained when samples of inhibited benzoles were incubated at 35°C. in containers of different metals and the time to form 10 mg. of gum per 100 ml. of benzole was determined.

These tests, carried out under much more drastic conditions than normal, indicate the direction in which the various metals, etc., affect inhibited motor fuels, rather than the extent, since experience has shown that under normal storage conditions—lower temperatures and larger ratio of volume to surface area—the effect of the material of the containing vessel is much less than indicated by laboratory-scale tests.

It has been claimed that certain compounds are capable of suppressing the effect of metal catalysts. According to Hansensche Mühlenwerke A.-G. (B.P. 409353, 1932) phosphatides of animal or vegetable origin, *e.g.* lecithin, stabilise petrols in the presence of cobalt oleate, which normally acts as an accelerator. Petrols which have been treated with copper salts for removal of mercaptans are liable to contain traces of copper, the catalytic effect of which is not counteracted by some of the usual inhibitors. According to F. B. Downing, R. G. Clarkson and C. J. Pederson (Oil Gas J. 1939, 38, No. 11, 97) the catalytic effect of the copper can be counteracted by the addition of certain organic compounds (metal deactivators), *e.g.* diisobutylidene-ethylenediamine, which are effective in concentrations as low as 5 parts per million.

The greater difficulty experienced in applying inhibitors successfully to blended motor-fuels containing alcohols, such as are used in many continental countries (R. Weller, Oel u. Kohle, 1934, 2, 527; Benzol-Verband, *ibid.* 1937, 13, 935) is admittedly due to the greater tendency of such blends to become contaminated with metallic catalysts (W. H. Hoffert and G. Claxton, 14<sup>th</sup> Int. Congr. Chim. ind. Paris, 1934).

**Preliminary Treatment of the Fuel.**—Although the direct addition of gum-inhibitors to some freshly-produced crude fuels stabilises them effectively, some mild preliminary treatment is usually necessary in order to obtain the best results. Moreover, treatment may be required for removing sulphur compounds, coloured and colour-forming, or malodorous constituents, etc.

Many crude fuels already contain phenolic and other compounds with inhibiting properties (W. H. Hoffert and G. Claxton, J.S.C.I. 1933, 52, 25T; E. Vellinger and G. Radulesco, Compt. rend. 1933, 197, 417; Ann. Off. nat. Comb. liq. 1934, 9, 499; F. Sager, J. Inst. Petroleum Tech. 1934, 20, 1044; E. Field, F. H. Dempster and

G. E. Tilson, Ind. Eng. Chem. 1940, 32, 489). These so-called "natural inhibitors," however, are usually far less effective than commercial inhibitors, and moreover, they may be present in excessive quantities and possess other disadvantages indicated above. Accelerating impurities, which are often present, are definitely objectionable, since the direct addition of inhibitors to such fuels may produce little effect or even increase gum formation. An example of the effect of accelerating impurities is given in fig. 7, showing the separate effects of increasing concentrations of cresol or thiophenol in a crude benzole as well as the effect of adding increasing amounts of cresol to the benzole when it already contained a definite amount of thiophenol (0.015%) (W. H. Hoffert and G. Claxton, Proc. World Petroleum Congr. 1933, 2, 69; see also C. D. Lowry, C. G. Dryer, C. Wirth and R. E. Sutherland, Ind. Eng. Chem. 1938, 30, 1275). Hence both inhibiting and accelerating impurities should be removed from

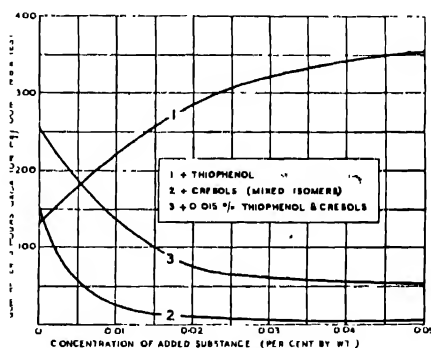


FIG. 7.

the fuel as completely as possible during the preliminary treatment.

(i) *Cracked Petrols.*—The following methods of treatment before addition of inhibitor are used (C. D. Lowry, C. G. Dryer, J. C. Morrell and G. Egloff, Oil Gas J. 1934, 33, No. 12, 8; W. B. Ross and L. M. Henderson, *ibid.* 1939, 37, No. 45, 107; W. W. Scheumann, *ibid.* 1939, 38, No. 25, 41):

- (1) Production of cracked petrol directly from cracking unit, and sweetening, *i.e.* removal of mercaptans.
- (2) Light acid-treatment of raw stock followed by redistilling and sweetening.
- (3) Splitting raw stock into a light and a heavy fraction, acid treating and redistilling the heavy fraction and sweetening the combined redistilled heavy and light fractions.
- (4) Clay-treating the raw stock to polymerise only the most unstable constituents and sweetening (M. R. Mandelbaum, Proc. World Petroleum Congr. 1933, 2, 21).

When a preliminary vapour-phase clay treatment is given, it is possible to run the clay much longer, giving a greatly increased yield. The

clay treatment removes colour, and polymerisation and removal of certain of the more active gum-forming constituents usually reduce considerably the quantity of inhibitor required (N. M. Steininger, *Ind. Eng. Chem.* 1934, **26**, 1039).

(ii) *Benzoles and Coal Spirits*.—For these types of spirit, the preliminary treatment may consist of one of the following (W. H. Hoffer and G. Claxton, *J.S.C.I.* 1933, **52**, 25T; *Proc. World Petroleum Congr.* 1933, **2**, 69):

- (1) Treatment with (a) caustic soda for removal of phenols and (b) dilute sulphuric acid (10–15%) for removal of pyridine bases, etc., and redistilling.
- (2) Treatment with 75–80% acid, for removal of colour and colour-forming compounds, and redistilling.
- (3) Treatment with fuller's earth, clay or other adsorbent (V. Voorhees, *Oil Gas J.* 1935, **34**, No. 30, 36).

When the sulphur content of the crude material is high, additional treatment for the removal of sulphur may be required. Carbon disulphide can be removed with negligible loss by (1) fractionation (Barbet column), (2) chemical processes (e.g. methanol-soda or ammonium polysulphide processes). When high amounts of thiophen, sulphides or disulphides are present, treatment with stronger acid may be necessary.

**Effect of Peroxide Formation on Inhibitors**.—Experience has shown that for maximum effectiveness, an inhibitor should be added to a fuel as soon after its preliminary treatment and redistillation as possible. If an unstable fuel is exposed to air without the addition of inhibitor, an inhibitor subsequently added is less effective. Some unstable fuels decrease in their response to inhibitors in a few days or even hours.

The first indication of the deterioration of a motor fuel is the formation of peroxides, their concentration having a direct relationship to the effectiveness of an inhibitor (J. A. C. Yule and C. P. Wilson, *Ind. Eng. Chem.* 1931, **23**, 1254). The deleterious effects of peroxides can be offset to some extent by increasing the amount of inhibitor. It is also possible to remove peroxides from some fuels and thus improve their "inhibitor response" (C. G. Dryer, C. D. Lowry, J. C. Morrell and G. Egloff, *ibid.* 1934, **26**, 885). If the fuel is kept longer, however, intermediate polymerised products or even gum may be actually formed, and it becomes impossible to stabilise the fuel effectively.

**Precautions and Methods of Adding Gum-Inhibitors** (Du Pont Tech. Bull. No. 4, 1934).—Gum-inhibitors are of three physical types: (a) liquids, which are readily miscible with motor spirits; (b) solids, which may be in the form of powder or granules; and (c) solutions of solids in inexpensive solvents, such as anhydrous methanol, cresylic acid, etc.

In view of the small quantity of inhibitor required (0.001–0.05%), care must be taken to obtain thorough solution and uniform distribution throughout the fuel.

In general, and regardless of whether the quantity of fuel to be treated is large or small,

experience has shown that the most satisfactory results are obtained by batch addition, that is adding a definite quantity of inhibitor to a given quantity of fuel followed by agitation or circulation of the contents of the storage tank. This is true whether or not the method of adding the inhibitor is of a proportioning type (*see below*).

**Liquids**.—Any system that is suitable for blending miscible liquids may be used. For example, the inhibitor may be added directly to the fuel in a storage tank, and the contents are then agitated or circulated by pumping out at the bottom and into the top or into a second tank. Alternatively, the liquid inhibitor may be run from a stock tank by means of a proportioning pump or other device into a stream of the fuel immediately after distillation, as it is delivered to a storage tank.

**Solids**.—For small batches of fuel, the solid inhibitor may be introduced directly into the storage tank of freshly-prepared fuel. Small portions of the total quantity required are added at a time, and the contents of the tank are thoroughly agitated by circulation or other means between each such addition. For larger batches, the inhibitor can be added on the suction side of the circulating pump, either in the form of a slurry with the fuel, or by means of a suitable mechanical feeding device, to a stream of fuel as it is pumped to storage. For these methods, the quantity of solid added should be well below the maximum that will dissolve in the fuel. In the second method, the pipe line to the storage tank should be sufficiently long to provide an opportunity for the inhibitor to dissolve in the fuel before reaching the storage tank. It is desirable to avoid solid inhibitor being carried into the tank, as it is difficult to agitate the contents sufficiently to pick it up again from the bottom.

The best method of dissolving the solid inhibitor in a fuel, when production is large enough to permit of more or less continuous operation, is to by-pass a stream of the fuel from a circulating pump upwards through a small tank containing the inhibitor and recirculating the fuel until all the inhibitor is in solution. A suitable apparatus is shown in fig. 8.

**Solutions of Solids in Liquids**.—These may be treated as already described for miscible liquids. Greater difficulty may be experienced, however, when using solutions owing to the fact that they contain materials that are sparingly soluble in the fuel. When such solutions are introduced into the fuel, precipitation of the inhibitor may occur initially, followed by re-solution in the fuel, and it is essential therefore that the solution be added uniformly and accompanied by rapid agitation. The best method is to inject the solution into the main fuel stream at a high pressure by means of a proportioning device with a small orifice.

The only other precaution necessary is to avoid leaving any residual alkali in the fuel to which the inhibitor is to be added, because, particularly with phenolic and aminophenolic inhibitors, it is apt to promote discoloration. This is probably due to the fact that the alkali catalyses the oxidation of the inhibitor, with the production of coloured secondary oxidation

products. Hence before adding inhibitors, all traces of alkali should be removed from the fuel by thorough washing with water or dilute acid. Similarly, when fuels are stored over water, the latter may be sufficiently alkaline to cause discoloration. In such cases it has been found beneficial to add to the water about 0.1% by wt. of sodium bisulphite or aluminium sulphate.

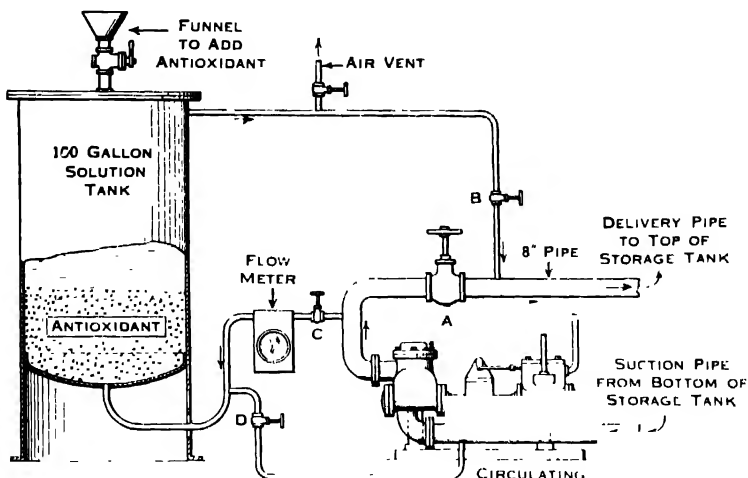


FIG. 8.

**Patents.**—The following incomplete list of British patents, relating to the use of inhibitors for stabilising motor spirits against gum and colour formation, is indicative of the wide variety of compounds that have been protected. For a survey of the U.S. patent literature up to February, 1937, see J. H. Byers (Nat. Petroleum News, 1937, 29, No. 11, 157; No. 15, 58). Up to the end of 1938, about 150 patents relating to gum and colour stabilisers for cracked petrols, benzoles, etc., had been issued in the U.S.A. Very few of the substances claimed, however, have been used commercially, and many of them appear to have little effect on the usual types of fuels and under ordinary conditions of storage.

Patent No.	Date.	Patentee	Inhibitor covered.
289347	27.10.26	P. G. Somerville and W. H. Hoffert.	Phenols and aromatic amines.
312774	30.4.28	Standard Oil Co.	Phenol, aromatic amine, urea or alkaloid.
318521	4.9.28	W. K. Lewis (Standard Oil Development Co.).	Aromatic amines, phenols and nitro-compounds, e.g. pyrogallol.
319362-3	21.9.28	H. G. M. Fischer and C. E. Gustafson (Standard Oil Development Co.).	<i>α</i> -Naphthol, <i>α</i> -naphthylamine, etc.
350438	5.3.30	Standard Oil Co.	Substituted aminophenol, e.g. <i>p</i> -benzylaminophenol.
364533	28.7.30	J. Hyman and G. W. Ayers.	Catechol and $\text{NH}_3$ or organic substituted ammonia.
383511	24.4.31	C. Willing, L. E. Sargent and J. F. Dudley (Standard Oil Development Co.).	Inhibitor and a coloured inhibitor, e.g. Indophenol Blue.
385066	21.11.30	C. L. Gutzeit (Standard Oil Development Co.).	Dyes such as indophenols, oxazines, etc.
388926	9.6.31	W. S. Calcott and H. W. Walker (E. I. Du Pont de Nemours and Co.).	<i>sec</i> -Arylamine, e.g. $\text{NHPh}_2$ .
394511	26.10.31	E. Ayres (Gulf Refining Co.).	Oxidation product of <i>α</i> -naphthol.
398219	7.3.32	F. B. Downing and H. W. Walker (E. I. Du Pont de Nemours and Co.).	Amine salts of phenols.

Patent No.	Date.	Patentee.	Inhibitor covered.
399733 404033	26 10.31 8 7.32	E. Ayres (Gulf Refining Co.). W. S. Calcott and H. W. Walker (E. I. Du Pont de Nemours and Co.).	Peri-mono-oxynaphthalene. <b>NN'</b> -diarylguanidine salt of a higher fatty acid.
406195	18.7 33	A. H. Stevens (Texaco Development Corp.).	<b>C</b> -alkylated polyhydric phenols.
406658	8.9.31	E. Ayres (Gulf Refining Co.).	Mixed inhibitors, <i>e.g.</i> $\alpha$ -naphthol and <b>NHPh</b> <sub>2</sub> .
408229	29.8 32	F. B. Thole and W. H. Thomas (Anglo-Persian Oil Co., Ltd.).	Polyhydric phenol dissolved in cresol.
409353	28.10 31	Hanseatische Muehlenwerke A.-G.	Animal or vegetable phosphatides.
410115	{ 18 12 31 11.3 32 }	C. D. Lowry and C. G. Dryer (Universal Oil Products Co.).	Hardwood tar.
417653	30 3.33	E. W. J. Mardles and W. Helmore.	Amino-compounds, <i>e.g.</i> urethanes, glycine with or without a phenol.
420371	26 5 32	J. W. Orelup.	Dinaphthylene oxide or perylene.
423938	10.8.33	E. W. J. Mardles and W. Helmore.	Derivatives of hydrazines or amines.
424582	24.8.32	E. I. Du Pont de Nemours and Co.	<i>p</i> -Hydroxyphenylaminoacetone nitrile and homologues.
430335	7.12.32	Wingfoot Corpn.	<i>p</i> -Methylamino- <i>p'</i> -aminodiphenyl ether, etc.
432121	20 1.33	E. I. Du Pont de Nemours and Co.	Dihydroxynaphthalenes, <i>e.g.</i> 1:5- <b>C</b> <sub>10</sub> <b>H</b> <sub>6</sub> ( <b>OH</b> ) <sub>2</sub> .
444026	24 1.34	E. V. Bereslavsky.	Pine oil treated with pyrogallol.
444585	21.9 33	E. I. Du Pont de Nemours and Co.	$\text{HO}-\text{R}-\text{N} \begin{array}{c} \diagup \text{CH}_2-\text{CH}_2 \diagdown \\ \diagdown \text{CH}_2-\text{CH}_2 \diagup \end{array} \text{O},$ <p><b>R</b> arylene nucleus.</p>
444894	26.9.34	Universal Oil Products Co.	Lignite tar fraction.
459722	12.7 35	Universal Oil Products Co.	Alkali-soluble fraction from tar, preferably L. T. tar.
459923	18.7.35	Universal Oil Products Co.	Inhibition of one fraction of fuel only.
462593	8 8 34	E. I. Du Pont de Nemours and Co.	<i>p</i> -Cyclohexylaminophenol.
467056	6.9.35	Wingfoot Corpn.	<i>sec</i> -Naphthylamine, <i>e.g.</i> phenyl- or tolyl- $\alpha$ - or $\beta$ -naphthylamine, at least partly hydrogenated.
470072	{ 5.2.36 7.10 36 }	I. G. Farbenind. A.-G.	Org. <b>N</b> compound and a phenol.
477745	25.4.36	N. V. Nieuwe Oetroot Mij.	Inhibitor after doctor treatment, alkali being removed by <b>NaHSO</b> <sub>3</sub> or <b>Al</b> <sub>2</sub> ( <b>SO</b> <sub>4</sub> ) <sub>3</sub> .
501844	17.8 36	Kodak, Ltd.	80-85% <b>N</b> -alkyl- <i>p</i> -aminophenol and 20-15% <b>N,N'</b> -di-alkyl- <i>p</i> -phenylenediamine.
503316	3.4.37	Kodak, Ltd.	Compounds of type <b>RCH</b> <sub>2</sub> <b>NHR'</b> <b>OH</b> , where <b>R</b> = alkyl and <b>R'</b> = phenylene with or without substituents.
503401	17.8.36	Kodak, Ltd.	Products from polyhydric phenols containing at least two <b>OH</b> groups in <i>o</i> - or <i>p</i> -positions, and primary or <i>sec</i> -alkyl-primary amine containing at least 4 <b>C</b> atoms.

**Bibliography.**—A. W. Nash and D. A. Howes, "The Principles of Motor Fuel Preparation and Application," 1935, Vol. II, p. 163 (Chap. XIII): The Formation, Estimation and Significance of Gum in Motor Fuels; "The Science of Petro-

leum," 1938, Vol. IV, p. 3033. Article by E. W. J. Mardles on Oxidants and Antioxidants in the Petroleum Industry; K. C. Bailey, "Retardation of Chemical Reactions," 1937 (Chap. XIV). W. H. H.



# INITIATORY EXPLOSIVES (r. Vol. IV, 535a).

**INK.** The word "ink" comes to us through the Latin *encaustum*, the name given to the pigment used for colouring baked tiles, and it is significant of this origin that the Ancient Egyptians wrote in carbon ink on potsherds which were afterwards baked (Fr. *encrer*; Ital. *inchiostrare*; Ger. *Tinte*). From this primary meaning the connotation of the word "ink" has been extended to include fluids that are employed for producing characters in writing or printing upon any material.

**Writing Inks.**—The earliest kind of writing ink was Indian or Chinese ink (*q.v.*), a solid preparation consisting of lampblack and glue. Liquid preparations containing carbon in suspension or colloidal form were afterwards introduced and were in use all over the world. In the West, carbon inks were gradually replaced by iron-gall inks; in this country the change occurred about the eighth or ninth century A.D. In the East, carbon inks are still in use, although in the principal cities, such as Cairo, they have practically disappeared. Lucas (Analyst, 1922, 47, 9) has published analyses of modern Egyptian carbon inks.

**Iron-Gall Inks.**—As first made, about the eighth century A.D., these consisted of an infusion of crushed galls or other form of tannin, mixed with a solution of copperas and sufficient gum arabic to keep the resulting colloidal iron tannate in suspension. Although spent tanbark, sumach and other sources of tannin are sometimes used in the manufacture of ink, galls have been found to be the most suitable raw material for the purpose.

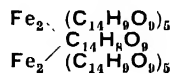
Aleppo or nut galls contain from about 50–80% of gallotannin, with amounts of gallic acid varying with the conditions of storage. Chinese galls usually contain about 60% of tannin (sometimes as much as 75%). Myrobalans (used for copying inks) contains 40–50% of tannin. For analyses of different kinds of galls and other tannin-producing materials, see Mitchell (*ibid.* 1923, 48, 2). Experiments made by Mitchell (*l.c.*) point to the conclusion that the pyrogallie group is the tinctogenic agent in both gallotannin and gallic acid; he has also shown (*ibid.* 1903, 28, 146; 1920, 45, 126) that the groupings (three hydroxyl groups in juxtaposition) found by Schluttig and Neumann ("Die Eisengalltintentein," Dresden, 1890, p. 16) to form iron inks will also yield inks in which ammonium vanadate or osmium tetroxide replaces the iron salt.

The tinctogenic value of galls or other sources of tannin thus depends upon the combined amount of gallotannin and gallic acid. For this reason determinations of tannin by the standard gelatin method used by leather manufacturers do not afford a true criterion of the value of the product for ink-making. It is necessary also to take into consideration the gallic acid present, determined, e.g. by Mitchell's colorimetric method (Analyst, 1923, 48, 2), in which the reagent consists of a solution of 1 g. of ferrous sulphate and 0.5 g. of sodium potassium tartrate in 100 ml. of water. The standard solution for

pyrogallol or gallic acid, and the total tinctogenic value of the substance under examination is expressed in terms of either pyrogallol or gallic acid. The tannin in the original solution is then precipitated with quinine hydrochloride and a colorimetric comparison is made with the filtrate; the difference between this result and that originally found gives the amount of gallic acid.

The old literature gives very divergent formulae for the relative amounts of galls and copperas to be used to obtain a permanent ink. Thus, Canevarius ("De Atramentis," 1660) prescribed 3 parts of galls to 1 of the iron salt, and Lewis ("Commercium Philosophico-technicum," 1763, p. 377) agreed with this. Other proportions recommended were 4:1 (Eisler, 1770), 5:1 (Reid, 1827), 1.5:1 (Brande), 2.4:1 (Ure), etc. All these proportions were obtained empirically with galls which probably contained very different proportions of tannin, and by methods in which different amounts of tannin were dissolved. But after allowance has been made for these factors, the balance of opinion is in favour of a proportion of about 3 parts of galls to 1 part of ferrous sulphate (*cf.* Mitchell, "Inks," 4th ed., C. Griffin & Co., London, 1937, p. 127).

This conclusion is supported by the experiments of Schluttig and Neumann (*op. cit.*, p. 44) and of Mitchell (Analyst, 1920, 45, 255) on the composition of the insoluble iron tannate formed on exposing a solution containing gallotannin and ferrous sulphate to the air. The deposits yielded from 7.8 to 8.6% of ferric oxide (5.5–6.6% of iron). The formula that agrees best with 5.5–6.6% of iron is that suggested by Schiff (Annalen, 1875, 175, 176):



In Mitchell's experiments the ratio between the amounts of iron and gallotannin in the spontaneously dried deposits was 1:16. This corresponds with a ratio of 1.3:2.2 between the ferrous sulphate and gallotannin.<sup>1</sup> Since, however, the amount of tannin varies with the substance employed, the table given on the next page will afford a guide to the approximate proportions of different tannin materials to be used with 1 part of ferrous sulphate.

A typical recipe for the manufacture of iron-gall ink of the old type is as follows: galls 120, copperas 80, gum arabic 80, water 2,400, phenol 6 parts.

The crushed galls are repeatedly extracted with water and the extracts are united and then mixed with the other ingredients. After mixing, the ink is allowed to mature in vats for several months.

**Iron Salts for Inks.**—Ferrous sulphate (copperas) has long been used as the most suitable salt for ink-making, but ferric chloride is used for gallic acid inks, and ferric sulphate chloride,  $\text{FeSO}_4\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (patented by Röhm and Haas

<sup>1</sup> For a discussion of the composition of the iron tannates formed when iron-gall ink dries on paper, see Mitchell, "Inks," 4th ed., C. Griffin & Co., London 1937.

Tannin material	Containing pure gallotannin per cent (circa).	Parts by weight required.
Commercial gallotannic acid	86	3.8
Aleppo galls . . . . .	62	5.0
Chinese galls (best) . . . . .	75	4.3
Japanese galls . . . . .	62	5.0
Acorn galls (Knopperrn) . . . . .	30	11.0
English oak-apple galls . . . . .	26	12.5
Chestnut wood . . . . .	9	36.0
Chestnut wood extract . . . . .	20	16.0
Sumach . . . . .	22	14.5
Valonia . . . . .	30	11.0
Divi-divi . . . . .	40	8.0
Myrobalans . . . . .	30	11.0

A.-G., (Chem.-Ztg., 1921, 45, 842) is employed to a limited extent. The advantages claimed for it are that it is not hygroscopic or deliquescent; that unlike ordinary ferric salts it does not act on aniline dyes, and, unlike ferrous salts, does not throw down a deposit when oxalic acid is used as the acid to render the ink stable.

Commercial copperas, as used for ink making, varies in colour from bluish-green or whitish-green to a bright grass green. On exposure to the air it gradually absorbs oxygen and becomes coated with a white layer which soon changes to yellowish-brown, owing to the formation of basic ferric sulphate. In this condition it is technically known as rusty and is usually regarded as of more value by ink manufacturers, probably because it accelerates the preliminary darkening of the ink in the vats.

The amount of iron in commercial copperas varies considerably. Fourteen samples examined by Mitchell (*op. cit.*, p. 121) contained from 18.14 to 25.92% of iron, and practical tests showed that an ink prepared from copperas with 18.8% of iron contained too little iron when the calculation had been based upon the use of copperas containing the theoretical 20%.

Commercial copperas is almost invariably acid. Thus five samples showed an acidity (in terms of N.-alkali solution) ranging from 0.11 to 0.37 ml. per gram. It is obvious that this acidity increases the amount of strong acid in the final ink and accounts for the acidity of inks to which no mineral acid has been added.

**Blue-Black Inks.**—The use of indigo to improve the colour of ink was mentioned by Eshler in 1770 ("Das Eshlerische Dntefass," Helmstadt, 1770, p. 28) and was used by Stephens in this country in 1836. In 1856 Leonhardi of Dresden patented an ink containing indigo and madder solution, and these inks were therefore termed "alizerine" inks, even after the madder had been discarded as superfluous. The new principle introduced was that of retarded oxidation. Whilst in the old type of iron-gall ink colour was given to the ink by partial oxidation in the vat, in "alizerine" inks a colouring matter is introduced to give a temporary colouring matter to the writing pend-

ing the formation of the insoluble violet-black iron tannate upon the paper. As mentioned above, indigo was at first the principal colouring matter used, but has now been partly or completely replaced by aniline dyestuffs, especially Soluble Blue. Gum, which was a constituent of the older type of ink, is not used in the more fluid modern blue-black inks.

The British Specification (H.M. Stationery Office) 1934, specifies for a Record Blue-Black Ink, that it must be a gallo-tannate ink containing not less than 0.5% nor more than 0.6% of iron, and that the ratio of iron to tannin substances shall be such as will ensure the highest degree of permanence in written characters.

A blue-black ink for general services and fountain pens must contain not less than 0.25% of iron. Like the record ink, it must yield a good blue-black colour after being blotted and give a deep black after 14 days. Both types of ink must remain clear and without appreciable deposit when evaporated to a fourth of the volume by exposure to the atmosphere. The acidity must be the least possible having regard to satisfactory performance of the inks.

**Gallic Acid Ink.**—The advantage of gallic acids inks over ordinary iron-gall inks is that, being already oxidised, they remain clear in the bottle. Hence they do not require the addition of acid to stabilise them, and so have little, if any, corrosive action upon steel pens. On the other hand, owing to the limited solubility of gallic acid (about 0.9% at 15°C.), these acid-free inks lack "body," and do not penetrate the paper so readily as the normal blue-black inks, which often contain more than 0.1% of free acid.

Originally gallic acid inks were prepared by hydrolysing Chinese galls to convert the gallotannin into gallic acid, but these were essentially mixed gallotannin and gallic acid inks, and gallic acid is now more generally used. Ferric chloride is used instead of copperas, and about 3% of an aniline dye and 0.1% of phenol are added.

**Copying Inks.**—These are concentrated iron-gall (blue-black) inks to which an ingredient, such as glycerin or dextrin, has been added to retard atmospheric oxidation of the ink upon the paper. Speaking generally, iron-gall copying inks should contain about 30–40% less water than inks of the same formula intended for ordinary writing purposes. The British Specification (H.M. Stationery Office) for blue-black copying inks requires the sample to contain not less than 0.6% of iron and to dry without stickiness and give a good clear copy 48 hours after writing. The ink must produce a good blue-black colour after being blotted and give a deep black after 14 days. Other requirements are the same as for ordinary blue-black inks (*supra*).

**Logwood Inks.**—Inks in which part of the galls is replaced by logwood chips or logwood extracts were at one time extensively used, especially on the Continent, but have now to a large extent been displaced by cheap blue-black and aniline inks.

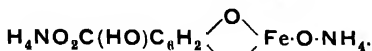
Chrome logwood inks (Dinglers Polytech. J. 1859, 151, 80) are also practically obsolete, at all events in this country, although still used in Germany. Walther (Chem.-Ztg. 1921, 45, 432) gives the following formula for a cheap ink of this

type: Logwood extract 24, hydrochloric acid (20° Bé.) 15, potassium dichromate 3, phenol 1, water 1,000 parts.

**Ink from Ammonium Ammonoxyferrigallate.**—Silbermann and Ozorovitz (Chem. Zentr. 1908, II, 1024) found that gallic acid reacts with ferric chloride to produce a chloro-ferrigallic acid,



and that this acid, when treated with ammonia, forms ammonium ammonoxyferrigallate,



This compound in a 7 or 8% solution can be used as a writing ink. The writing is violet-black at first, but becomes black in a few hours, and is sufficiently oxidised in 30 minutes not to be removable by water. According to Zimmermann, Weber and Kimberly (J. Res. Nat. Bur. Stand. U.S.A. 1935, 14, 465) a solution of ammonium ammonoxyferrigallate (20 g. per litre) forms an ink that flows well and leaves no sediment after exposure to the air for a month. It is recommended as a satisfactory record ink.

**Lignone Sulphonate Inks.**—The lignone sulphonates in the waste liquor from the manufacture of cellulose pulp by the sulphite process combine with iron salts to form black compounds which resemble iron tannates and dry on paper as insoluble black pigments. Hence, black and blue-black inks can be made from these waste liquors, and during the last few years such inks have become commercial products. Whilst they have many excellent qualities, the experience of many years will be necessary to prove that these inks will be as permanent as properly made iron-gall inks.

**Coloured Writing Inks.**—Formerly these inks consisted of suspensions or solutions of pigments, such as verdigris, and natural colouring matters such as cochineal. They are now almost exclusively made from aniline dyestuffs. The following are coloured writing inks of the old type:

**Red Ink** was formerly prepared from Brazil wood or extract of Brazil wood, with the addition of alum or stannous chloride, *e.g.*

(1) Brazil wood 280, tin-salt 10, gum 20 parts; boiled with 3,500 parts of water and evaporated down until the required depth of colour is attained.

(2) Extract of Brazil wood 15, alum 3, tin-salt 2, tartaric acid 2, water 120 parts.

Cochineal or carmine inks are prepared by boiling cochineal in water, precipitating the carmine with alum and tin salt and dissolving this in the requisite amount of strong ammonia. Another method is to dissolve 2 parts of ammonium carbonate in 200 parts of water and macerate for 3–4 hours with 40 parts of cochineal and 2 parts of alum.

Most of the red inks now used are solutions of magenta or eosin in water, together with a little gum. Glycerin also is added if the ink is to be used for copying.

**Blue Ink.**—In the older type of blue ink Prussian blue was the colouring matter commonly employed. The pigment was placed in an earthen vessel and either strong hydrochloric acid, nitric acid or sulphuric acid was added to it. After the mixture had remained 2 or 3 days, much water was added, and after settling, the supernatant liquor was drawn off from the sediment. The sediment was well washed until the wash liquor was free from iron and free acid, after which it was dried and mixed with oxalic acid in the proportion of 8 parts of Prussian blue to 1 part of acid. The pigment was dissolved in sufficient water to bring it to the required intensity.

An excellent blue ink can be made by dissolving 10 parts of indigo-carmin and 5 parts of gum in 50–100 parts of water. Solutions of blue aniline dyes may be used, but are easily effaced by bleaching agents and some fade on exposure to light.

Typical modern coloured writing inks consist of solutions of the following dyestuffs:

**Blue.**—Soluble Prussian Blue (0.5%), sodium indigo sulphonate (0.1%), Methylene Blue (0.5%), Bavarian Blue 18F (1.2%).

**Green.**—Acid Green (1.2%), Malachite Green (0.2%).

**Red.**—Macerate S (0.5%), Fuchsin F (0.2%), Eosin A (1.5%).

**Violet.**—Methyl Violet (0.3%).

**Brown.**—Alizarin (2.5%) and ammonia solution (1%). Dries brown.

For table of systematic tests for these and other coloured inks, see Lunge, "Technical Methods of Analysis," 1914, in, 1, 529, and Mitchell (*op. cit.*).

**State of Massachusetts Official Ink.**—

This is a standard ink for comparative tests, and contains the following ingredients: Dry gallotannin, 23.4; gallic acid crystals, 7.7; ferrous sulphate, 30; gum arabic, 25; dilute hydrochloric acid, 25; phenol, 1, in 1,000 parts of water. This formula is based on that given by Schluttig and Neumann (*op. cit.*).

**"League of Nations" Ink.**—At a meeting of the National Research Council at Ottawa, September, 1932, a Report by the League of Nations on the Permanence of Papers was accepted; this Report included recommendations as to the requirements of a permanent ink. These comprised the following, *inter alia*:

(1) The ink must be thin and flowing, and keep in a non-stoppered bottle.

(2) It must dry quickly and must not be sticky, even immediately after drying.

(3) It must not be acid enough to attack pen or paper, or show any tendency to spread over the paper.

(4) It must contain sufficient iron and tannin, so that when dry it will turn black, will not fade in light, and will resist water and alcohol.

"Art. 46.—Ink for documents shall be black, free from aniline or corrosive materials, and resistant to light and decolorising substances.

"Only the ferro-gallic inks are accepted as 'normal,' and they must comply with the following conditions:—

"(1) Be clear, fluid, not acid enough to attack the pen, nor have a tendency to spread on the

paper; have a lasting colour, and produce a writing which dries quickly without stickiness.

"(2) Contain not less than 5 g. of iron per litre.

"(3) Be completely indehible in 15 days.

"(4) Produce a dark colour and be as resistant to light, air, water and alcohol as an ink composed of 23.4 g. of tannin, 7.7 g. of crystallised gallic acid, 30 g. of iron sulphate, 10 g. of gum arabic, 2.5 g. of concentrated hydrochloric acid and 1 g. of carbolic acid, made up to 1 litre. The inks are tested according to the regulations of the Bureau of Control and Standards."

It may be pointed out that some of these requirements are contradictory. An ink containing 0.25% of conc. aqueous hydrochloric acid will attack pens, and an acid-free ink (which will not corrode pens) will not comply with the requirements for tannin and gallic acid.

**Prussian Regulations for Official Tests of Ink.**—According to the Prussian regulations of May 22, 1912, inks are classified into (1) "documentary," and (2) "writing inks," the latter being subdivided into (a) iron gall inks, and (b) logwood and dyestuff inks. (1) A "documentary ink" is defined as an iron-gall ink which gives dark writing after 8 days' exposure to light and air. It must contain at least 27 g. anhydrous gallotannic and gallic acids, and 4 g. iron (calculated as the metal) per litre. On the other hand, the amount of iron must not exceed 6 g. so that the ratio of gallotannic plus gallic acid to iron must lie within the limits 4.5:1 and 6.75:1. The ink must not alter for at least 14 days in the ink-pot, and must flow readily from the pen. The writing done with it must not be sticky immediately after drying, and after 8 days it must remain deep black when washed with water and with alcohol (85 and 50%). (2) Iron-gall "writing inks" must contain at least 18 g. gallotannic and gallic acids, and at least 2.6, and not more than 4 g. iron per litre (ratio 4.5:1 and 6.75:1). In other respects they must comply with the requirements of "documentary inks." Inks of Group (b) are not officially tested.

For the American standards for iron writing, duplicating and cancelling inks, their composition, manufacture and methods of testing, see U.S.A. Bureau of Standards, 1920, Circular No. 95 (for Abstract, see *Analyst*, 1921, 46, 61).

**Examination of Writing Inks.—Acidity.**—A rapid method of determining corrosive acids in ink has been devised by Mitchell (*ibid* 1921, 46, 131). 10 ml. of the ink are repeatedly distilled with excess of sodium acetate and the acetic acid in the distillates is titrated with standard alkali.

Another method of determining both the added mineral or oxalic acid and the weak organic acids is to bleach the pigments in the ink with boiling hydrogen peroxide and titrate the liquid with N-alkali (phenolphthalein as indicator). The alkalinity of the glass bottles used for ink may sometimes neutralise the acidity of the ink and cause deposits to form (Mitchell, *op. cit.*, 184, 224).

**Ash.**—Iron-gall inks differ considerably in the readiness with which the carbon can be burned off. Cautious addition of a few crystals of ammonium nitrate facilitates the ignition.

Typical English inks have been found to yield from 0.42 to 2.52% of mineral matter.

**Iron.**—The ash is dissolved in dilute hydrochloric acid, and the iron is oxidised with hydrogen peroxide and precipitated with ammonia. Or the volumetric method prescribed in the Prussian Official Tests may be used: the ash from 10 ml. of ink is dissolved in 1–2 ml. of hydrochloric acid (sp.gr. 1.124), the solution is evaporated to dryness with 1 to 2 ml. of chlorine water, the residue is treated with 0.5 ml. of hydrochloric acid to dissolve basic iron salts, and the solution is cooled and diluted with 20 ml. of water. About 1 g. of potassium iodide is added, and the iodine liberated at 55° is titrated with N./10 thiosulphate solution, the solution being cooled before the starch indicator is added.

Mitchell (*Analyst*, 1908, 33, 81) analysed a large number of English writing-inks and found that, although the composition of any one manufacturer's ink remained fairly constant over long periods, there were marked differences between the inks of different manufacturers. The total solid matter ranged from 1.89 to 7.91%, the ash from 0.2 to 2.52%, and the iron from 0.18 to 1.09%.

**Gallotannin and Gallic Acid.**—A mixture of 10 ml. of the ink with 10 ml. of concentrated hydrochloric acid is shaken with successive portions of 50 ml. of ethyl acetate until the aqueous layer gives no reaction for gallotannin or gallic acid after treatment with sodium carbonate and addition of ferric chloride and ferrous sulphate. A special form of shaking apparatus, devised by Rothe, is suitable for the extraction. The ethyl acetate extract is shaken several times with semi-saturated potassium chloride solution (10 ml. each time) to remove iron salts, and then evaporated *in vacuo*; the residue is taken up with a little water, transferred to a weighed crucible and dried at 105–110°, or preferably *in vacuo* at about 60°, until constant in weight. In the Prussian Regulations the residue is regarded as gallotannin and gallic acid when 0.1 g. thereof absorbs in the presence of 2 g. of sodium bicarbonate at least 0.5 g. of iodine. If less iodine is absorbed the ink is not up to official requirements. In determining the iodine absorption about 0.1 g. of the residue is mixed in a stoppered flask with 2 g. of sodium bicarbonate and 25–50 ml. of a standard solution of iodine (about 50 g. per litre), and the flask is closed and allowed to stand overnight, after which the unabsorbed iodine is titrated with standard thiosulphate.

A more accurate determination of gallotannin and gallic acid may be made by Mitchell's colorimetric method (*Analyst*, 1923, 48, 1).

**Gums and Dextrin.**—10 ml. of the ink are treated with 20 ml. of 95% alcohol, and the precipitate is collected on a counterpoised filter, dried and weighed.

**Glycerin.**—The total solids of the ink are treated with 96% alcohol and the alcoholic extract is evaporated and tested for glycerin, e.g. fumes of acrolein on heating with potassium bisulphate (*v. Vol. V*, 302c).

**Phenol and Salicylic Acid.**—The residue from the ink is mixed with sand and extracted with ether. On evaporating the ethereal extract phenol may be recognised by its odour and by

giving a precipitate with bromine water. Salicylic acid is detected by the violet colour obtained with ferric chloride (r. Vol. II, 570b).

**Dyestuffs.**—The ink is slightly acidified with hydrochloric acid and boiled for 15 minutes with a thread of wool or cotton. The threads are thoroughly washed with hot water, and if they have been dyed they are boiled in sodium carbonate solution or acidified water, and the dyestuffs are again fixed on cotton or wool and identified by systematic tests for dyes (cf. Vol. IV, 156–172).

**Indigo Carmine** is fixed upon wool and redissolved by an alkaline bath. In alkaline solution it remains bright blue after addition of sulphuric acid, but is changed to green by hydrochloric acid.

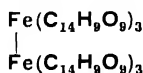
**Testing the Writing.** Pieces of standard paper are stretched in a frame inclined at an angle of 45°, and a definite amount of ink made to flow down them from a pipette fixed in a special position with regard to the paper. At the same time a parallel test is made upon the same paper with Schluttig and Neumann's standard iron-gall ink containing 23.4 g. gallotannic acid, 7.7 g. crystalline gallic acid, 30 g. ferrous sulphate, 10 g. gum arabic, 2.5 g. hydrochloric acid, and 1 g. phenol per litre. This ink is allowed to stand for at least 4 days at 10–15°, and decanted from any deposit. For comparison in the test it is coloured with a suitable dyestuff to match the ink under examination. The paper with the colour stripes of the two inks upon it is exposed to the air for 8 days in diffused daylight, and is then cut horizontally into strips which are immersed in water, 50% alcohol and 80% alcohol respectively. No perceptible bleaching of the ink should take place (Hinrichsen, Chem.-Ztg. 1913, 37, 265; Mitchell, *op. cit.*, p. 207).

**Age of Ink in Writing.**—The change in the colour of ink on paper proceeds rapidly at first, then very slowly, and is usually complete in the course of a few months. If the colour of the writing changes in the course of a few days, the ink is comparatively recent (see Mitchell, *op. cit.*, p. 207).

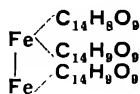
Another test depends upon the fact that as the ink becomes oxidised it is gradually converted into a resinous tannate, which retains the dyestuff. Thus if a dilute acid is applied to writing a few months old the ink will run, whereas if the ink is some years old it will be hardly affected by the reagent.

Mezger, Rall and Heess (Chem.-Ztg. 1931, 55, 481) have devised a method based on the gradual diffusion of the salts in the ink-writing into the adjacent paper. Their "chloride pictures" and "sulphate pictures" enable a judgment to be formed of the relative age of the ink. The precautions to be observed in drawing conclusions from the "pictures" have been discussed by Heess (Arch. Kriminol. 1935, 96, 13; also Mitchell, *op. cit.*, p. 213).

It is probable that in oxidised ink the iron exists as the first in the series of tannates,



described by Wittstein (Jahresber. 1849, 28, 221) and by Schiff (Annalen, 1875, 175, 176). See also Silbermann and Ozorovitz, l.c.). As the oxidation proceeds the successive precipitates contain more iron, and eventually approximate in composition to



obtained by Pelouze by prolonged exposure of a solution of ferric sulphate and gallotannic acid to air (Mitchell, Analyst, 1920, 45, 247).

**Ink Powders.**—Owing to their convenience for use by travellers, ink powders and tablets are being increasingly used. Some, when dissolved, approximate in composition to gallotannate inks, whilst others consist of aniline dyestuffs.

A violet logwood-ink powder described by Dieterich ("Pharmazeutisches Manual," 10th ed., 1909, p. 646) consists of logwood extract 100, aluminium sulphate 40, potassium oxalate 60, potassium bisulphate 20, potassium chromate, 4, salicylic acid 1.5 parts.

**Aniline Ink Powders.**—Viedt in 1875 recommended the use of Nigrosine, which was to be dissolved in 80 parts of water.

Dieterich (*op. cit.*) gives the following formulae for ink powders of different colours:

**Black Ink Powder.**—Aniline Green D 9.0  
Ponceau 2R 8.0, Phenol Blue 1 part.

**Red Ink Powder.**—Ponceau Red 2R.

**Green Ink Powder.**—Aniline Green.

**Violet Ink Powder.**—Phenol Blue 1.5,  
Ponceau 2R 2 parts.

**Violet Copying-Ink Powder.**—Methyl Violet 20, sugar 10, oxalic acid 2 parts.

The British Specifications (H.M. Stationery Office) for Blue-Black Ink Powder, require the ink made up from the powder to contain not less than 0.25% of iron, and the ratio of iron salt to tannin substances to be such as will ensure a satisfactory degree of permanence. The ink must produce a good blue-black colour after being blotted, and give a deep black after 14 days.

**Gold and Silver Inks** are prepared from gold and silver, or from cheaper substitutes such as bronze powder and Dutch leaf. The leaf metal, mixed with honey, is carefully ground down to the finest possible condition; it is then well washed and dried. A suitable medium preparation consists of 1 part of pure gum arabic and 1 part of soluble potash glass in 4 parts of distilled water. As a rule, 1 part of the powder is sufficient for 3 or 4 parts of the medium.

Imitation silver ink is best made by rubbing up aluminium foil or powder with gum.

**Sympathetic or Secret Inks.**—These preparations are devised to trace words or figures which are invisible when written but become visible when subjected to heat or appropriate chemical reagents. Examples: a weak infusion of galls is colourless on paper, but becomes black when moistened with a solution of copperas; and if a weak solution of copperas be used, the

writing will be invisible, until the paper is moistened with a weak solution of galls. Equal parts of copper sulphate and sal ammoniac dissolved in water form a colourless ink, the writing of which turns yellow on the application of heat. Weak solutions of silver nitrate or of auric chloride when exposed to the sunlight become dark brown and purple respectively. Solutions of cobalt chloride or nitrate give tracings which become green or blue when heated and disappear again as the paper cools.

**Ink for India-rubber Stamps.**—The following preparation produces ink adapted for this purpose. It does not easily dry upon the pad, and is readily taken up by the paper: Aniline colour in solid form (blue, red, etc.) 16, boiling distilled water 80, glycerin 7 parts. The colour is dissolved in the water, and the other ingredients are added whilst agitating. The "*carbon papers*" used for giving two or more copies of written or typed matter are coated on one side with a mixture of, for example, yellow wax and tallow containing a suitable pigment such as lampblack or Prussian blue, or some aniline colour.

**Indelible or Safety Inks.**—Compositions passing under these names consist of finely divided carbonaceous substances, such as Indian ink or lampblack, held in suspension in a glutinous or resinous liquor. They are devised so as to resist the action of strong acid or alkaline solutions. An ink having these properties may be made of Indian ink rubbed into ordinary writing ink.

A suspension of lampblack in sodium silicate solution makes an excellent safety ink, but has the disadvantage that it must be kept in air-tight bottles.

Vanadium ink is prepared very simply by adding a small proportion of ammonium vanadate to a filtered decoction of galls. It is a deep black ink, which flows freely from the pen and is not easily removed without destruction of the paper.

**Copying Ink or Indelible Pencils** (v. Vol. III, 359).

**Hektograph Inks** are used to give a large number of copies, and must therefore contain a concentrated colouring matter. The original is written on ordinary paper with the ink and is laid face-down on a sheet of a composition of glue and glycerin (about 1:5) until the ink has been absorbed into the surface of the composition. By applying sheets of paper with slight pressure, 60 to 100 copies can then be obtained.

A typical ink contains: a water-soluble blue dye 10, glycerin 10, water 50–100 parts.

Dyes not easily soluble in water or glycerin are first dissolved in alcohol and then mixed with the other ingredients. Thus a red hektograph ink may contain: magenta 20, alcohol 20, acetic acid 5, gum 20, water 40 parts; or magenta 10, alcohol 10, glycerin 10, water 50 parts.

**Ticket-Writer's Ink** is made of good black ink, with liquid gum added to produce a gloss.

**Ink for Writing on Glass** is a solution of gum arabic in strong hydrofluoric acid coloured with some matter which can withstand the action of the acid: cudbear is used for this purpose.

**For Enamelled Cards** ordinary printing ink (mainly a mixture of lampblack and oil) is mixed with a few drops of equal parts of copal varnish and mastic varnish.

**Lithographic Ink** ought to conform to the following requirements. It should be flowing on the pen, not spreading on the stone; capable of forming delicate tracings, and very black to show its delineations. The most essential quality of the ink is to sink well into the stone, so as to reproduce the most delicate outlines of the drawing and to afford a great many impressions. It must therefore be able to resist the acid with which the stone is moistened in the preparation, without letting any of its greasy matter escape.

Lithographic ink may be prepared as follows: mastic (in tears) 8 oz., shellac 12 oz., Venice turpentine 1 oz.; melt together; add wax 1 lb., tallow 6 oz.; when dissolved, add a further 6 oz. of hard tallow soap in shavings; and when the whole is perfectly incorporated, add 4 oz. of lampblack; lastly, mix well, put in moulds, and when cold cut it into square pieces.

Another recipe is as follows: melt together wax 18, soap 18, shellac 14, resin 6, tallow 10 parts. Then stir in 2 parts of india-rubber dissolved in 5 parts of oil of turpentine, and 6 parts of lampblack. Heat the whole until the smell of turpentine has nearly disappeared and then cast into sticks.

Autography is the operation by which a writing or a drawing is transferred from paper to stone. For autographic ink: mix white wax 8 oz and white soap 2–3 oz.; melt and add lampblack 1 oz.; mix well, heat strongly, and add shellac 2 oz.; again heat strongly and stir well. On the mixture cooling pour it out as before. With this ink lines may be drawn of the finest and fullest class, without danger of spreading; and the copy may be kept for years before being transferred. These inks are rubbed down with a little water in the same way as Indian ink.

**Printing Ink.**—Ink prepared for use with type, copper-plates, etc., consists of a medium and pigment. The chief properties required in a good printing ink are:

- (1) A perfectly uniform syrupy consistence.
- (2) Must be easily transferred from the ink-rollers to the type, and from the type to the paper.
- (3) Must not smudge types, and must be easily washed off them with printer's lye.
- (4) The ink must not dry so quickly as to set on types or rollers, but must not dry so slowly on the paper as to hinder folding, etc., of sheets.
- (5) When dry, the ink must not "set off" from the paper on to anything with which it comes in contact.
- (6) The printed characters should not show a greasy margin.
- (7) The ink should not have a strong odour.

The ink which most nearly fulfils all these requirements is composed of the finest quality of lampblack incorporated with a pure linseed oil varnish. (For methods of examining lamp-blacks and carbon blacks, see Neal and Perrott, U.S. Dept. of the Interior, Bureau of Mines,

Bull. No. 192, 1922, 72; also British Standards, Nos. 284, 286, 287, 288.) The demand for cheap inks for the printing of newspapers and cheap books has been met by using cheaper qualities of lampblack and substituting for the varnish various mixtures of oils and resins with soap, which may or may not contain a proportion of linseed oil.

The linseed-oil varnish used for good ink was formerly prepared by heating linseed oil in a boiler until the vapour evolved could be ignited. A light was then applied and the whole allowed to burn for about half an hour, until a trial showed that the oil was of the right consistence. The practice of burning the oil gave a dark-coloured product and has now been discontinued.

The present practice is to heat the oil to about 380–400°, taking every precaution to avoid its ignition. The boiler is provided with a closely fitting lid, or, better, with a cover of wire-gauze, which extinguishes a flame while allowing the vapours to escape.

Provision is made for lifting the boiler from the fire or withdrawing the fire from the boiler, or, in some apparatus, for running off the oil into a cold vessel. A gutter round the furnace above the fire-door prevents any chance of the oil reaching the fire, even should it boil over the top of the pot. In some modern plant the oil is heated by means of superheated steam. A varnish so prepared is insoluble in water or alcohol, but mingles readily with fresh oil and unites with mucilages into a mass diffusible in water in an emulsoid form. The oil loses from one-tenth to one-eighth of its weight by boiling into the thick varnish.

Letterpress ink of average quality may be made by reheating a varnish produced as described above and adding for each gallon of the original oil 4 lb. of rosin and 1 lb. of brown soap in slices. This is then mixed with the requisite quantity of pigment—for lampblack rather less than one-third of its weight—and the whole is thoroughly ground and incorporated in a suitable machine, usually between rollers of polished granite or steel, as in Lehmann's apparatus. The presence of soap in the ink causes it to "lift" well, *i.e.* to be completely transferred from the type to the paper. The following recipes are typical of inks of a cheaper class:

*Linseed Oil and Rosin Vehicle.*—Rosin 50, boiled linseed oil 100, rosin soap 10, partly boiled oil 6 parts by weight.

*Rosin Oil Vehicle.*—Rosin oil 50, rosin 50, boiled linseed oil 50, rosin soap 5, thin boiled linseed oil 6 parts.

*Cheap Mineral Oil Vehicle.*—Rosin is dissolved in about an equal weight of heated mineral oil (petroleum of sp.gr. 0.880–0.920; Wass, *l.c.* P. 322298, 1902).

*Composition Vehicles.*—Venice turpentine 5, castor oil 15, white wax 1 kg. These are mixed at 100° (Knecht); then 9 kg. of thick turpentine, 10 kg. of soft soap and 4 kg. of "oleïne," mixed hot, are added (Rösl).

The lampblack used is of various qualities according to the price of the ink. The propor-

tion should be just sufficient to give a full black impression; it is less with the better qualities of lampblack. The ink for rotary machines contains about 28% of lampblack, that for high-speed newspaper-printing about 24%, that for book printing about 21%, and that for illustration work about 19% with 2% of Prussian blue and 1% of indigo.

Other inks consist of 25 parts of paraffin oil, 45 parts of fine colophony and 15 parts of lampblack. The amount of colophony is reduced in soft inks for high-speed work.

It has been proposed to use oxides of iron or manganese as black pigments for printing ink (*see e.g.* Fireman, U.S.P. 802928, 1905). Paper printed with such ink could be bleached and subsequently made into white paper. This could not be done with the lampblack inks now used.

It is said that so extremely thin is the layer of ink on small type that 1 lb. wt. even of cheap newspaper ink will cover not less than 7,000 sq. ft. of type matter.

**Coloured Printing-Inks.**—These inks are made from the varnishes above described by the addition of dry colours, taking great care that the colours are thoroughly well ground and assimilated with the varnish, since lumps of any kind not only clog the type but alter the tint. Some tints which are exceedingly light will require an admixture of white powder to give the necessary body to the ink.

The following pigments are eligible for incorporation in printing inks:

*White.*—Heavy spar (barium sulphate), zinc white and titanium white.

*Red.*—Orange lead, vermilion, burnt sienna, Venetian red, Indian red, lake vermilion, orange mineral, rose pink and rose lead.

*Yellow.*—Yellow ochre, gamboge and lead chromate.

*Blue.*—Cobalt blue, Prussian blue, indigo, Antwerp blue, Chinese blue, French ultramarine and German ultramarine.

*Green.*—Usually mixtures of yellow and blue, but sometimes chrome green, cobalt green, emerald green or terre verte.

*Purple.*—A mixture of those used for red and blue.

*Deep Brown.*—Burnt umber with a little scarlet lake.

*Pale Brown.*—Burnt sienna; a rich shade is obtained by using a little scarlet lake.

*Lilac.*—Cobalt blue with a little carmine added.

*Pale Lilac.*—Carmine with a little cobalt blue.

*Amber.*—Pale chrome with a little carmine.

*Pink.*—Carmine or crimson lake.

*Shades and Tints.*—A bright red is best obtained from pale vermilion with a little carmine added; dark vermilion when mixed with the varnish produces a dull colour. Orange lead and vermilion ground together also produce a very bright tint, and one that is more permanent than an entire vermilion colour. Cheaper substitutes are orange mineral and rose pink, and red lead. Lead chromate affords the brightest colour. For dull yellow yellow ochre is used. Indigo is excessively dark and requires a good deal of trouble to lighten it. It makes a fine

showy colour when brightness is not required. Prussian blue is useful, but it dries very quickly, hence the roller must be frequently cleaned. The objection to Prussian, Antwerp and Chinese blues is that they are hard to grind and likely to turn greenish with the varnish when used thin. For green any of the yellows and blues may be mixed. The varnish itself having a yellow tinge will produce a decidedly greenish tint with a small quantity of Antwerp blue. Emerald green is made by mixing pale chrome with a little Chinese blue, and then adding the mixture to the varnish until the tint is satisfactory.

In using painter's colours it is advisable to avoid the heavy ones as much as possible. Some colours require less oil in the varnish than others.

A bronze of changeable hue may be given to inks with the following mixture (Southward): gum shellac 1½ lb. is dissolved in 1 gallon of 95% alcohol or Cologne spirits for 24 hours and 14 oz. Aniline Red then added. After standing for a few hours the mixture will be ready for use. When added to good blue, black or other dark ink, it imparts a rich hue. The quantity must be carefully apportioned.

**Reflex Blue Lakes.**—The pigment known as "Reflex Blue" is prepared from the carbonium dye, Alkali Blue, by precipitation from an aqueous solution with hydrochloric or sulphuric acid in presence of lead acetate. The most precipitate is incorporated with a lithographic varnish, and, after standing for the water to separate, the lake is ground into ink. These lakes get their names from the bronze effect obtained when they are mixed with lithographic varnish.

**Monastral Fast Blue BS.**—An insoluble blue dyestuff pigment of a new type has been introduced under this name (see R. P. Lustead *et. al.*, J.C.S. 1934, 1016-1039). It is insoluble in water, oils, alcohol and many organic solvents. The same pigment is made in Germany and sold under the name of Helbogen Blue B (Chem.-Ztg. 1936, 60, 375). It can be used in admixture with yellow pigments to produce greens brighter than the ordinary Brunswick greens. Unlike cobalt blue, it is relatively opaque to infra-red rays (Mitchell and Ward, Analyst, 1936, 61, 754).

**Rotagravure Inks.**—The principle of the "rotagravure" process is the reverse of that used in half-tone work, the printing surface being an intaglio composed of minute rectangular cells of varying depth. These cells, numbering about 40,000 to the sq. in., are filled with the ink, the excess of which is removed by means of a steel blade or "doctor," so that films of graduated depth are left in the cells on the cylinder of the rotary press. When the web of paper is pressed against the mouths of the cells the ink is lifted from them and transferred to the surface of the paper, and the density of the deposited pigment corresponds with the amount of ink in the respective cells. The ink required for the process differs in its properties from ordinary printing ink. It must be capable of being removed completely from the cells, must be fairly transparent, and must not yield deposits. These requirements are met by using special media containing balanced proportions

of fixed and volatile ingredients, and by the use of pigments which are thoroughly ground. Special mills are required for grinding the mixture of pigment and medium, and the ink is passed through a hair sieve before being used in the printing machine.

Rotagravure inks made with an oil basis require thinning with benzine or carbon tetrachloride, whilst those with a water basis have the drawbacks that they smudge readily and are not waterproof. A waterproof ink prepared by Albert (Penrose's Annual, 1932) is free from these drawbacks; the medium consists of water and water-soluble organic pigments incorporated with a solution of rosin soap.

An asphalt ink particularly suitable for intaglio printing has been patented by Winship (B.P. 334370, 1929). The asphaltic base (*e.g.* from gilsonite *q.v.*) is diluted with a petroleum solvent and an oily resin; the emulsion is stabilised with glue and finally incorporated with water and a suitable pigment.

**Patent Inks for Cheques.**—Numerous printing inks for cheques have been made with the object of revealing any attempt to remove writing from the surface of the paper. One of the best known of these inks is that of Hehner and Dupré (B.P. 375, 1881). The preparation used for printing the note consists of a sulphide (insoluble in water, but acted on by dilute acids, *e.g.* zinc sulphide), with lead carbonate or other salt of a heavy metal. The mixture is made into a paste with glycerin, treacle and gum arabic, and can be used for printing invisible characters on the cheque, or added to the coloured paste used for printing the ground-work. Dark stains are immediately produced when acid, alkali or a cyanide solution is applied to the cheque.

In the ink patented by Waterlow & Sons and Clifford (B.P. 292393, 1927) a substance fluorescing in ultra-violet light, but the fluorescence of which is destroyed by ink-erasing agents, is claimed. In a later patent (B.P. 417488) claim is made for the use of water-insoluble substances for this purpose.

**Examination of Printing Inks.**—The behaviour of a printing ink in practice is of much more importance than its composition. For methods of analysis, see Tuttle and Smith, J. Ind. Eng. Chem. 1914, 6, 659. Specifications for the tests to be applied to inks used in the U.S. Government Printing Office have been published. These include tests for the following properties: (1) non-separation of oil from pigment; (2) cleanness of transfer; (3) hardness; (4) drying properties; (5) offset or smudging; (6) colour; (7) quantity required for an average 5,000 printed pages.

**Arsenic in Printing Ink.**—As a result of the detection of arsenic in the printing on wrappers used for bread (Eladon, Analyst, 1924, 49, 336), Barry (*ibid.* 1927, 52, 217) suggested limits for the proportions of arsenic to be permitted in the pigments used in printing inks, and classified these pigments into three groups:

- (1) those to be used unconditionally, containing less than 1 part of arsenic in 50,000 of pigment;



(II) containing between 1 in 20,000 and 1 in 50,000, to be used in conjunction with those in Class I;

(III) those containing more than 1 part in 20,000, which are to be rejected.

These suggestions were adversely criticised by Morrell and Smyth (*ibid.* 1927, 52, 339) as too stringent in view of the amount of arsenic that would be present in the final ink.

**Bronzing.**—The production of printed matter having the colour and lustre of gold or silver, is carried out by printing with a varnish which remains "tacky" for a time, and then dusting over the whole surface with bronze powder or aluminium powder or similar substances. The powder adheres only to the varnish and thus produces the desired effect.

Such a varnish may be produced by melting into a good linseed oil varnish sufficient beeswax to give it the consistence of lard or tallow. (See Ure's Dict. of Arts, Manufactures, etc.; Cooley's "Cyclop. of Practical Receipts"; Lehner's "Ink Manufacture"; Southward's "Practical Printing"; Noble's "Principles and Practice of Colour Printing"; L. E. Andes' "Oil Colours and Printer's Inks"; Mitchell's "Inks: Composition and Manufacture"; Seymour's "Modern Printing Inks.")

**Marking Inks.**—Natural marking inks, such as those prepared from the juice of the *Coriaria thymifolia* (the ink-plant of New Granada) and the juice of the Indian marking nut (*Semecarpus anacardium*), are not only used locally, but also form the basis of commercial preparations. The juice of *Rhus toxicodendron* ("the poison ivy") and that of *Rhus venenata* ("the poison sumach") are also employed in the manufacture of black varnish and of marking inks.

**Chemical Marking-Inks.**—The inks of this type most commonly used are those containing a silver salt the reduction of which within the fibres of the fabric leaves an insoluble black pigment. In the earliest inks of this type the liner had first to be treated with a *pounce* (e.g. sodium carbonate in gum mucilage) and then dried, but these have been completely superseded by inks in which the reduction is effected by heat.

Redwood's marking ink, which is still the prototype of certain modern marking inks, was prepared by adding a solution of 31 parts of silver nitrate in water to an aqueous solution of 50 parts of sodium carbonate, collecting and washing the precipitated silver carbonate, triturating it with tartaric acid, and adding sufficient ammonia to dissolve the silver tartrate. The ink was then completed by the addition of 15 parts of archil extract, 16 parts of white sugar and 50 parts of gum arabic.

An analysis by Mitchell of a British silver marking ink of this type gave the following results: water (containing 4.87% of ammonia), 76.93; total solids, 23.07; mineral matter, 12.30; silver, 9.98; platinum, 0.26 tartaric acid, 6.83; gum, 3.94%. The ink contained archil as a temporary pigment.

Various modifications of silver marking-inks have been published, and the addition of certain other metals to the ink has been claimed in different patents.

**Aniline Marking-Inks.**—Two types of these marking inks are sold. In the older type there are two solutions which are kept separate until just before use. These are to a large extent similar to Jacobsen's aniline ink (Dinglers Polytech. J. 1867, 183, 78):

(a) *Copper Solution.*—Copper chloride, 8.52 g.; sodium chlorate, 10.65 g.; ammonium chloride, 5.35 g.; water, 60 ml.

(b) *Aniline Solution.*—Aniline hydrochloride 20 g., dissolved in 30 ml. of water and mixed with 20 g. of a solution of gum arabic (1:2) and 10 g. of glycerin.

For use, 1 part of (a) is mixed with 4 parts of (b). The writing, which is green at first, gradually blackens as aniline black forms within the fibres of the fabric. Steaming accelerates the blackening, but dry heat tends to make the marked place brittle. Finally the marked place is washed with soap and water which renders the ink a deep blue-black.

As this process is relatively tedious, there has been an increasing demand, especially by laundries, for one-solution writing and stamping inks which do not necessitate preliminary mixing, and produce markings which do not require to be steamed or washed.

In some of these inks the aniline salt and oxidising agent are so balanced that oxidation does not take place within the bottle. Several inks made on this principle were patented by Grawitz (F.P. 276397, 1898). One of them contains: (a) aniline oil, 110 ml.; hydrochloric acid (20 B<sub>é</sub>), 100 ml.; water, 100 ml.; (b) potassium ferrocyanide, 150 g. in 300 ml. of boiling water. The two solutions are mixed, cooled and added to a solution of 60 g. sodium chlorate in 400 ml. water.

In some of these inks the stage of retarded oxidation has not been reached, for after keeping fluid for months they may suddenly gelatinise in the bottle.

Other one-solution inks contain an aniline black dyestuff dissolved in aniline oil or in mixtures of aniline and its homologues. The exact composition and methods of preparing these inks are carefully guarded as trade secrets.

**Examination of Marking Inks.**—The composition of a marking ink is of subsidiary importance to its behaviour in practical tests. The main requirements of a good marking ink are: (1) it must not injure the fibres of the fabric; (2) it must flow smoothly from a pen, but not "run" when applied to linen; (3) the marking must darken rapidly when treated with a moderately hot iron or otherwise; (4) the marking must not fade when repeatedly washed with soap and water, and must resist the action of acids, alkalis and bleaching agents; (5) the ink must be stable in the bottle and not gelatinise or form deposits if the cork is not replaced for some time.

**Marking Ink Pencils.**—The earliest type of pencil devised for marking linen consisted of a silver salt incorporated with a suitable basic material and a provisional colouring matter (Dunn, B.P. 2316, 1858). In other pencils (Hickisson, B.P. 9149, 1884) one end had a marking point composed of a mixture of silver nitrate fused with gum and potassium nitrate,

whilst the other end was a mordant (e.g. borax, wax and pyrogallol) which was applied to the writing to fix it.

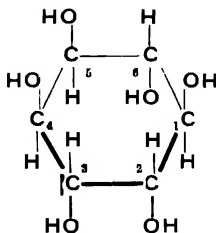
Aniline dyestuffs soluble in oil are claimed by Hickisson (B.P. 5316, 1893) as the colouring matter in marking-ink pencils. For this purpose they are incorporated with a suitable medium such as gum tragacanth, kaolin and borax. Some of the aniline marking-ink pencils now sold produce characters that are very fugitive.

Organic pigments are now to be obtained rivalling the most permanent mineral pigments in fastness. Thus Indanthrene Blue G, after exposure to the air for 18 months was found to be as permanent, though not quite so brilliant, as cobalt blue.

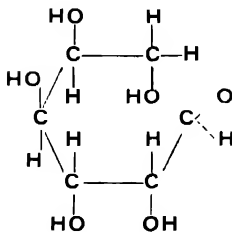
C. A. M.

#### INOSINASE (v. Vol. IV, 315a).

**INOSITOL.**—Several polyhydroxy-cyclohexanes occur naturally, and of these the inositols are the best known. They are hexahydroxycyclohexanes (hexitols). Nine stereoisomers of this formula are possible, according to the positions of the hydroxyl groups on each



*l*-Inositol.



*l*-Mannose.

carbon atom, relative to each other and to the plane of the ring. For convenience, the above structure of *l*-inositol is expressed by the

symbols  $\begin{smallmatrix} 1 & 4 & 5 \\ 2 & 3 & 6 \end{smallmatrix}$  indicating that the hydroxyl

groups attached to carbon atoms 1, 4, and 5 lie above the plane of the ring, and those attached to carbon atoms 2, 3 and 6 lie below the plane. Using this shorthand, the theoretically possible

stereoisomers are:  $\begin{smallmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 3 & 4 & 5 & 6 & 1 \end{smallmatrix}$ ,  $\begin{smallmatrix} 1 & 2 & 3 & 4 & 5 \\ 2 & 3 & 4 & 5 & 6 \end{smallmatrix}$ ,

$\begin{smallmatrix} 1 & 2 & 3 & 4 & 1 & 2 & 3 & 5 & 1 & 2 & 4 & 5 & 1 & 2 & 3 & 1 & 3 & 5 & 2 & 3 & 6 \end{smallmatrix}$

$\begin{smallmatrix} 1 & 4 & 5 \\ 2 & 3 & 6 \end{smallmatrix}$  4 6 ' 3 6 ' 4 5 6' 2 4 6' 1 4 5'

Other variations will be found upon

examination to be identical with one of these structures. In particular, it should be noticed that in one case only is the mirror image non-

coincident;  $\begin{smallmatrix} 2 & 3 & 6 \\ 1 & 4 & 5 \end{smallmatrix}$  cannot be made to coincide

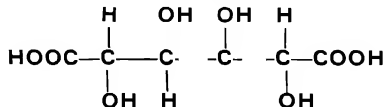
with  $\begin{smallmatrix} 1 & 4 & 5 \\ 2 & 3 & 6 \end{smallmatrix}$ , and these two are therefore optical isomerides. The other isomers are inactive.

Of these nine possible structures, four only have been isolated. These are *d*- and *l*-inositol, *meso*- or *i*-inositol, and scyllitol. All occur naturally, either free or combined. All have closely similar chemical properties. They are white crystalline solids, readily soluble in water, sparingly soluble in alcohol. Like the sugars they have a sweet taste, and in fact are isomeric with the hexoses, having the molecular formula  $C_6H_{12}O_6$ . From the formulae of *l*-mannose and *l*-inositol given above, the transformation of a hexose to an inositol would appear to be a simple aldol change, but such a reaction has not yet been carried out *in vitro*. A reaction of this type is, however, postulated in a series of changes recorded by Michael, Ruhkopf and Suckfull (Ber. 1935, 68 [B], 1523).

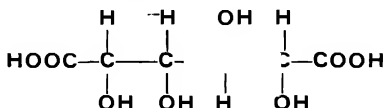
*d*-Inositol (*matezodambrose*).—M.p. 247–248°,  $[\alpha]_D +65^\circ$  (in water), occurs as the monomethyl ether in *Pinus lambertiana*. Demethylation with hydriodic acid yields *d*-inositol. Its chemical properties are typical of other inositols. Thus, it forms hexa-acetyl and hexabenzoyl derivatives. It reduces ammoniacal silver nitrate but not Fehling's solution, and does not mutarotat. The monomethyl ether, *pinitol*, found in *P. lambertiana*, occurs also in senna leaves and in Madagascan rubber latex and has m.p. 186°,  $[\alpha]_D +65^\circ$ . The structures of *d*- and *l*-inositol are discussed immediately below.

*l*-Inositol.—M.p. 247°,  $[\alpha]_D -65^\circ$ , occurs as a monomethyl ether, *quebrachitol*, in quebracho bark and in rubber latex. Demethylation with hydriodic acid yields *l*-inositol (Tanret, Compt. rend. 1889, 109, 908). Quebrachitol is a white crystalline solid, m.p. 190°,  $[\alpha]_D -80^\circ$ .

The structural formulae of *d*- and *l*-inositol are readily assigned, since of the nine possible stereoisomers two only are optically active and enantiomorphs. One of these is shown above (*l*-inositol); the other is its mirror image. These structures are in agreement with the isolation of both mucic acid,



and *d*-saccharic acid,



on oxidation of *l*-inositol with permanganate (Posternak, Helv. Chim. Acta, 1936, 19, 1007). The configurations assigned are not absolute but are dependent upon the convention used in the sugar series.

**Racemic, *dl*-Inositol.**—M.p. 253°, can be formed by mixing equal weights of *d*- and *l*-inositol, and occurs naturally in mistletoe berries

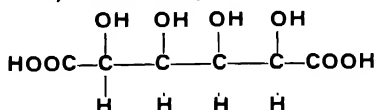
and in blackberries. It is, of course, inactive (Tanret, Compt. rend. 1907, 145, 1196).

*i*-Inositol (*mesoinositol*, *dambrose*, *nucite*) is the isomer most commonly found in nature. It occurs in muscle, heart, lungs and liver and many other human and animal organs. In plants it is also widespread, especially in leaves (*asparagus*, oak, ash, walnut, etc.), frequently esterified with phosphoric acid (e.g. *phytin*). The large-scale isolation from the steep-waters from the preparation of corn starch has been described by Hoglan and Bartow (Ind. Eng. Chem. 1939, 31, 749). A monomethyl ether, *bornesitol* (m.p. 199°) is found in *Borneo rubber*; a dimethyl ether, *dambonitol* (m.p. 195°) has been isolated from *Gaboon rubber*. An isomeric monomethyl ether, *sequoyie*, has been isolated from *redwood* (Sherrard and Kurth, J. Amer. Chem. Soc. 1929, 51, 3139).

*i*-Inositol is a white crystalline solid, m.p. 225°, optically inactive and non-reducing. The following derivatives have been described: the *hexa-acetate*, m.p. 212°, the *monobromo-inositol penta-acetate*, m.p. 240°, *tribromo-inositol tetra-acetate*, m.p. 140° or 235°, and the *inositol-dibromohydrin*, m.p. 210° (Müller, J.C.S. 1907, 91, 1780; see also Griffin and Nelson, J. Amer. Chem. Soc. 1915, 37, 1555); the *hexapropionate*, m.p. 100°, the *hexa-n-butyrate*, m.p. 81°, the *hexa-isobutyrate*, m.p. 181°, the *hexa-n-valerate*, m.p. 63°, the *hexa-isovalerate*, m.p. 147°, and the *hexa-3:5-dinitrobenzoate*, m.p. 86° (Hoglan and Bartow, l.c.). On oxidation with nitric acid (*d* 1.4) it yields the ketone *inosose* (pentahydroxycyclohexanone), m.p. 198–200° (Posternak, Helv. Chim. Acta, 1936, 19, 1333).

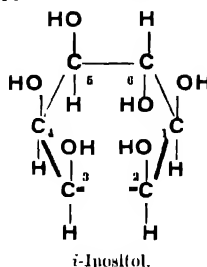
The allocation of a structural formula to *i*-inositol is difficult. Since it is optically inactive, the structures  $\frac{2\ 3\ 6}{1\ 4\ 5}$  and  $\frac{1\ 4\ 5}{2\ 3\ 6}$  (see above) may be ruled out; in fact, they belong to *d*- and *l*-inositol. Seven possibilities remain, and these are reviewed by Posternak (Compt. rend. 1929, 188, 1296). The following considerations enable a formula to be suggested:

(a) A tetraphosphate of *i*-inositol with a negative rotation has been prepared. This fact excludes structure  $\frac{1\ 2\ 3\ 4\ 5\ 6}{0}$ . (b) An inactive monophosphate is known (Anderson, J. Biol. Chem. 1915, 20, 480, 495). This excludes structure  $\frac{1\ 2\ 3\ 4}{5\ 6}$ . (c) The action of fuming nitric acid on mono- and di-phosphates of *i*-inositol gives both racemic and inactive tartaric acids. These could not be obtained from the structure  $\frac{1\ 3\ 5}{2\ 4\ 6}$ . (d) Oxidation with alkaline permanganate at 0° gives among other products, allomucic acid,



Of the remaining structures, this acid can only be obtained from  $\frac{1\ 2\ 3\ 4\ 5}{6}$ .

The structure of *i*-inositol would therefore appear to be:



This configuration is supported by more recent work by Posternak (Arch. Sci. phys. nat. 1941, v, 23, Suppl. 44). *Acetobacter suboxydans* oxidises *i*-inositol to give a keto-group at C<sub>3</sub>, and on further oxidation (KMnO<sub>4</sub>-Na<sub>2</sub>CO<sub>3</sub>) *dl*-succharic acid is formed, establishing the structure of the ketone. The latter on catalytic reduction (H<sub>2</sub>-PtO<sub>2</sub>) yields *i*-inositol quantitatively. If sodium amalgam is used for the reduction, *scyllitol* is also formed (see below).

*i*-Inositol has been found to promote the growth of bacteria and other organisms, including yeast. In this connection it has been called "*bios I*." A review of these accessory growth factors has been given by Koser and Saunders (Bact. Revs. 1938, 2, 99) (*v. Growth-Promoting Substances*, this Vol., p. 138).

A hexaphosphate of *i*-inositol, *phytic acid*, occurs as an alkali salt (*phytin*) in plants and plant seeds (see Posternak, Compt. rend. 1919, 169, 139; Helv. Chim. Acta, 1921, 4, 150; Anderson, J. Biol. Chem. 1915, 20, 496).

*Scyllitol* (*cocositol*, *quercinitol*), m.p. 349°, is a fourth stereoisomer of the inositol group. It has been found in organs of the dog-fish (*Scyllium canicula*) and in the cocoanut palm (*Cocos species*) and in *Acanthus vulgaris*, *Cornus florida*, etc. Recent work by Posternak (l.c. 1941) indicates that *scyllitol* differs from *i*-inositol only in the configuration around C<sub>3</sub>.

The preparation of other isomers has been reported from the action of acids on *i*-inositol (Müller, J.C.S. 1912, 101, 2393) and by reduction of the ketone *inosose* (Posternak, Helv. Chim. Acta, 1936, 19, 1333). Little is known of these products.

An X-ray examination of *l*- and *i*-inositol and of *quebrachitol* has been made (Patterson and White, Z. Krist. 1931, 78, 76; White, *ibid.* 80, 1).

For the detection of inositols, Scherrer's reaction is used (Annalen, 1852, 81, 375). Evaporation with nitric acid and then with ammoniacal calcium chloride yields a rose-red coloration if 0.0005 g. of inositol is present. The estimation of inositols in the presence of glucose, using periodic acid, is described by Fleury and Joly (J. Pharm. Chim. 1937, 26, 341, 397). D. W. Woolley (J. Biol. Chem. 1941, 140, 453) determines *i*-inositol by its growth-promoting effect upon yeast preparations.

#### PENTITOLS.

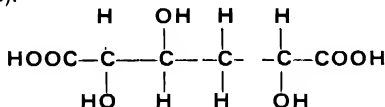
Owing to their close relationship to the inositols (hexitols), the pentahydroxycyclo-

hexanes (pentitols) may be mentioned here. Of the sixteen possible stereoisomers of this formula, two only are known, both optically active. They are named *d*- and *l*-quercitol, but they are not enantiomorphous. This nomenclature is therefore unfortunate, since enantiomorphs may well be found.

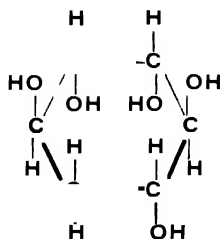
*d*-Quercitol,  $C_6H_{12}O_5$ , m.p.  $234^\circ$ ,  $[\alpha]_D^{20} + 24^\circ$  (in water), is found in acorns and to a small extent in the leaves and bark of the oak. It has also been isolated from the leaves of *Chaetumrops humilis* Linn., the European member of the palm family (H. Müller, J.C.S. 1907, 91, 1766). The presence of five hydroxyl groups is shown by the formation of a penta-acetate and pentanitrate. It is reduced by hydriodic acid to a mixture of aromatic derivatives, including benzene, phenol, pyrogallol and quinone, and also to hexane.

The structure of *d*-quercitol has been the subject of communications by Karrer (Helv. Chim. Acta, 1926, 9, 116), Kiliani and Scheibler (Ber. 1889, 22, 517; 1931, 64 [B], 2473) and Posternak (Helv. Chim. Acta, 1932, 15, 948). The isolation of mucic acid from the products of oxidation by nitric acid (Kiliani) agrees with structures expressed by the arrangements  $\begin{smallmatrix} 2 & 5 & 6 & 2 & 5 & 6 \\ 1 & 4 & & 3 & 4 \end{smallmatrix}$ , or

their mirror images,  $\begin{smallmatrix} 1 & 4 & 3 & 4 \\ 2 & 5 & 6 & 2 & 5 & 6 \end{smallmatrix}$  (see above for explanation of the notation). Posternak (*loc.*) oxidised *d*-quercitol with alkaline permanganate at  $0^\circ$  and isolated metasaccharonic acid (yield 19%) from among the products. This acid he identified by degradation of the corresponding aldono-lactone (metasaccharin) to *d*-2-deoxyxylose (Levene and Mori, J. Biol. Chem. 1929, 83, 803).



Metasaccharonic acid.



The structure of *d*-quercitol follows, but it is, of course, dependent upon the convention which allocates the configuration of *d*-glucose. It may be noted that *d*-quercitol is a deoxy-*d*-inositol.

*l*-Quercitol, m.p.  $174^\circ$ ,  $[\alpha]_D - 74^\circ$  (in water), occurs in the leaves of *Gymnema sylvestre*. It is not the enantiomorph of *d*-quercitol and its structure is not known.

G. T. Y.

**INSECT WAX** (Chinese Wax, Chinese Insect Wax) is the secretion of an insect, *Coccus*

*ceriferus* Fabr. (*C. pela* Westwood), which infests the bark and twigs of the "evergreen tree," *Ligustrum lucidum* Ait. growing in Western China. It should not be confused with the so-called "China wax," the Chinese variety of oriental beeswax, *v. Guedda Wax*.

E. I.

**INSECTICIDE EMULSIONS** (v. Vol. IV, 301d).

**INSULARINE.** Insularine has been isolated together with a second base from the root of *Cissampelos insularis* Makino (Fam. Menispermaceae) by Kondo and Yano (J. Pharm. Soc. Japan, 1927, 47, 107). *C. ochaiiana* Yamamoto also contains insularine (Kondo and Tomita, Arch. Pharm. 1936, 274, 76).

*Insularine*,  $C_{37}H_{38}N_2O_6$ ,  $[\alpha]_D^{25} + 27.95$ , m.p.  $166^\circ$ , is amorphous and easily soluble in  $Et_2O$  (thus separated from accompanying base). It contains three methoxyl and two *N*-methyl groups, the three remaining oxygen atoms occur probably in ether linkages. The Hoffmann degradation of the methiodide yields an  $\alpha$ -methine, m.p.  $115^\circ$ ,  $[\alpha]_D^{25} + 110.6^\circ$ , and a  $\beta$ -methine, m.p.  $185^\circ$ . Further degradation yields a *N*-free compound, m.p.  $208^\circ$  and  $[\alpha]_D^{25} + 73.37^\circ$ , needles from ether.

The constitution of insularine is still unknown; for absorption spectrum, see Ochiai, J. Pharm. Soc. Japan, 1929, 49, 425.

Insularine belongs to the group of the bisco-claurine alkaloids (v. Vol. III, 230c) which contain 2 mol. of substituted benzyltetrahydroisocoumolines joined together by one or several oxygen-bridges. To the same chemical group belong *dauricine* (*q.v.*), *oxycaanthine* (v. Vol. I, 683c), *berbamine*, *tetradrine*, *phanthine*, etc. For survey on this group, see Kondo and Tomita (*loc.*).

Schl.

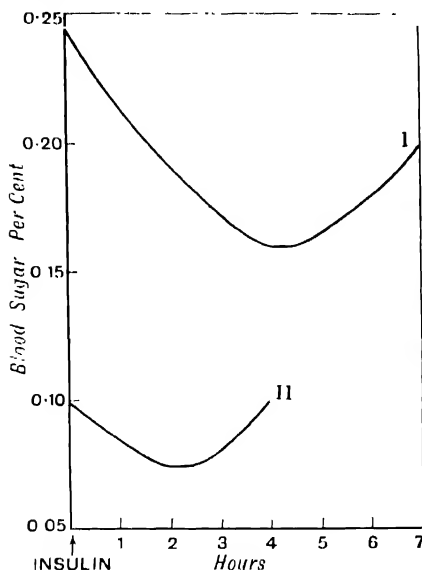
**INSULIN, THE ANTIDIABETIC**

**HORMONE.** Insulin is a protein hormone from pancreas and is an important factor in the metabolism of carbohydrate in the body. When injected into the normal (curve II) or diabetic (curve I) animal it produces a temporary decrease in blood sugar.

It is used for the amelioration of the symptoms of *diabetes mellitus*, the cause of which may be a failure of the pancreas to supply enough insulin for the needs of the body. Symptoms of this disease include hunger, thirst, polyuria and muscular weakness. The blood sugar is high, and glucose, often accompanied by acetoacetic acid, acetone and  $\beta$ -hydroxybutyric acid, is excreted in the urine.

Removal of the pancreas was shown by von Mering and Minkowski (Arch. exp. Path. Pharm. 1890, 26, 371) to cause diabetic symptoms. The occurrence of diabetes when the main gland was removed was prevented by grafting a portion of the pancreas on to the abdomen. They postulated that *diabetes mellitus* is caused by the absence from the body of a principle essential for carbohydrate metabolism. In mammalian pancreas there co-exist zymogenous tissue, supplying an exocrine secretion which passes through the pancreatic duct into the duodenum, and a number of microscopic islets, first described by Langerhans, whose cells

are the source of the endocrine secretion of insulin into the blood stream. These islets are frequently in anatomical continuity with the zymogenous tissue. Until 1921 many unsuccessful attempts were made to obtain pancreas extracts which would be active by oral administration or by injection to diabetics. These failures may have been due to the destruction of insulin by the proteolytic enzymes of pancreatic juice which are present in aqueous extracts of the whole gland. On this assumption Banting and Best (J. Lab. clin. Med. 1921-22, 7, 251, 464) ligated the ducts in dogs, thus bringing about the degeneration of the zymogenous tissue. The dogs were then killed and their pancreas ground with sand and Ringer's solution.



The extract was heated and the liquid filtered and when injected into depancreatized dogs produced a rapid decrease in glycaemia or glycosuria. Banting and Best also succeeded in preparing active extracts from fetal calves' pancreas at a stage before the fifth month of gestation when the endocrine insulin secretion is already active while the exocrine enzyme secretion has not yet been formed. In certain fishes (*Teleostei*) the islet tissue occurs apart from the zymogenous tissue and Macleod (J. Metab. Research, 1922, 2, 149) prepared active extracts from this tissue.

The use of aqueous alcohol by Collip (J. Biol. Chem. 1923, 55, xl-xli) and aqueous acid alcohol by Doisy, Somogyi and Shaffer (*ibid.* 1923, 55, xxxi), made possible a commercially practicable process for the production of insulin from whole ox-pancreas. Salting out and isoelectric precipitation of the insulin protein to the partial exclusion of other proteins provide methods of purifying it. Moloney and Findlay (J. Chem. Physics, 1924, 28, 402) adsorbed insulin on charcoal and then digested the charcoal with benzoic acid in 60% alcohol. The more easily adsorbed

benzoic acid replaced the insulin, which was recovered by evaporating the alcohol and extracting the aqueous insulin solution with ether to remove excess benzoic acid.

Dudley (Biochem. J. 1923, 17, 376) purified crude insulin by precipitating the active material from aqueous solution by picric acid and subsequently regenerating the hydrochloride from the picrate by alcoholic hydrochloric acid.

#### PREPARATION.

A typical method of preparing insulin is that employed by the Toronto workers, Scott and Parker (Trans. Roy. Soc. Canada, 1932, [iii], 26, V, 311)<sup>1</sup>:

100 lb. of fresh ox pancreas freed from excess fat and connective tissue are cooled to 4°C. as soon as possible after slaughter. The glands are minced and dropped into 25 gallons 95% alcohol (ethyl, denatured with 10% methyl alcohol), 5 gallons water and 1,200 ml. conc. HCl. The mixture is agitated for 1 hour and then allowed to stand overnight. The liquid is then drawn off by centrifuging and the residue re-extracted with an amount of 60% alcohol equal in volume to the liquid removed during the centrifugation. The combined extracts are adjusted to  $pH$  8 with ammonia, filtered and the filtrate re-acidified by adding 140 ml. of conc.  $H_2SO_4$  to each 50 gallons of solution 300 gallons of such acidified filtrate are evaporated to about 40 gallons in a vacuum still at a vapour temperature not exceeding 25°. After distillation, the concentrate, at  $pH$  2, is quickly heated to 50° and filtered to remove the coagulated lipid. After filtering and cooling to 30° the active material is then salted out by the addition of sodium chloride to a concentration of 25%. The crude protein from 600 lb. pancreas is then dissolved in 30 litres of water and reprecipitated by sodium chloride at a concentration of 15%. The precipitate, weighing about 150 g., is readily dissolved in 5 litres water containing 10 ml. of 8-N-HCl. Thersol to 0.3% concentration is added to four such combined lots of solution, the reaction is adjusted to  $pH$  5 by adding 5N-NaOH and the mixture is kept at 2° for one week. The active precipitate which separates is removed and dissolved in 7 litres of distilled water containing sufficient  $H_2SO_4$  to make the reaction  $pH$  2. To this liquid 4 vol. of absolute alcohol are added slowly with stirring. After standing at room temperature for 2 days, the precipitate is separated and rejected, and to every 6.5 litres of liquor are added 3.5 litres of absolute alcohol and 10 litres of ether. The precipitated insulin, after standing with the solution at room temperature for 2 days, is removed, dissolved in 8 litres of distilled water and the solution adjusted to  $pH$  5. The resulting active precipitate is removed and dissolved in 16 litres of distilled water containing enough HCl to make the reaction of the solution  $pH$  2.8. This solution is sterilised by means of a Sautz filter and the potency assayed. The yield of insulin is about 2,000 units per kg. pancreas, but varies according to the quality of pancreas employed.

<sup>1</sup> A more recent method is described by Romans, Scott and Fisher in Ind. Eng. Chem. 1940, 32, 908.

Fisher and Scott (J. Biol. Chem. 1934, **106**, 305) found that the insulin content of cattle pancreas decreases with increasing age of the animal.

Animal		Units per kg
Foetal calves	5 months	29,200-38,800
" "	5 7 "	21,100-24,900
Calves "	6 8 weeks	10,400-12,800
Cattle "	2 years	3,900-6,100
Cows	9	1,700-2,000

#### PROPERTIES

**Crystalline Insulin.**—Abel (Proc. Nat. Acad. Sci. 1926, **12**, 132) first described crystalline insulin which he obtained in the form of microscopic rhombohedra by dissolving insulin in weak acetic acid and removing contaminating impurities by precipitation with brucine. After adding m./6 pyridine to the clear solution there

was produced on standing a precipitate of crystalline and amorphous insulin. Harington and Scott (Biochem. J. 1929, **23**, 384) described an improved method of preparing insulin crystals by the use of saponin and precipitating with ammonia. The crystalline insulins obtained by Abel and by Harington and Scott using their own and Abel's method were submitted to careful assay by Culhane, Marks, Scott and Trevan (*ibid.* 1929, **23**, 397), using different methods; the results showed variation according to the method used from 20 to 27 international units per mg.

Insulin salts such as hydrochloride, sulphate, picrate have not been crystallised but are readily obtained as amorphous powders. Scott (*ibid.* 1934, **28**, 1592) found that the crystals contain zinc and that traces of salts of zinc, cadmium, nickel and cobalt facilitate crystallisation and showed, moreover, that electrolysed insulin of low ash content could not be induced to crystallise without the addition of traces of these metals. He elaborated a method of crystallisation by adding insulin to a



WEDGE-SHAPED INSULIN CRYSTALS.

phosphate buffer containing 10% acetone and a salt of zinc, the insulin concentration in the mixture being about 0.1%; adjustment of the mixture to  $p_H$  6 resulted invariably in production of crystals or crystals and amorphous insulin (in the latter case the crystals can be separated from the amorphous by gentle centrifuging).

Scott (Trans. Roy. Soc. Canada, 1932, [iii], **26**, V, 275) succeeded in obtaining two forms of crystalline insulin, a wedge-shaped form from aqueous acetone acetate buffer at  $p_H$  5.2 and the more usual rhombohedra from the same procedure at  $p_H$  6. The crystals were identical

in composition and potency. Insulin is, therefore, dimorphous.

**Physical.**—Insulin hydrochloride forms a white powder, non-deliquescent and readily soluble in water. Adjustment of the aqueous solution to  $p_H$  5.5 causes the formation of an isoelectric precipitate which Wintersteiner and Abramson (J. Biol. Chem. 1933, **99**, 741) found to have a constant solubility in m./30 acetate buffer at  $p_H$  4.8-6.5 of 0.0004%. The isoelectric precipitate is readily soluble in all acids and alkalis although high concentrations of the former reprecipitate it with loss of potency. Crystalline insulin dissolves readily

in dilute acid and with difficulty in alkali. Insulin is soluble in phenol, cresol, formamide, strong aqueous solutions of amides, anhydrous liquid ammonia and aqueous acetone and alcohol below 80°. It is insoluble in pyridine, alcohol, acetone, ether, chloroform, ethyl acetate, xylene, benzene, toluene, propyl, butyl and amyl alcohols, petroleum and most other anhydrous organic solvents. High temperatures in aqueous solution cause inactivation and it is more unstable in alkaline than in acid solution. Heating to 100° in the dry state has little effect. According to Krogh and Hemmingsen (Biochem. J. 1928, 22, 1231) the half-life period of insulin at pH 4 at various temperatures is:

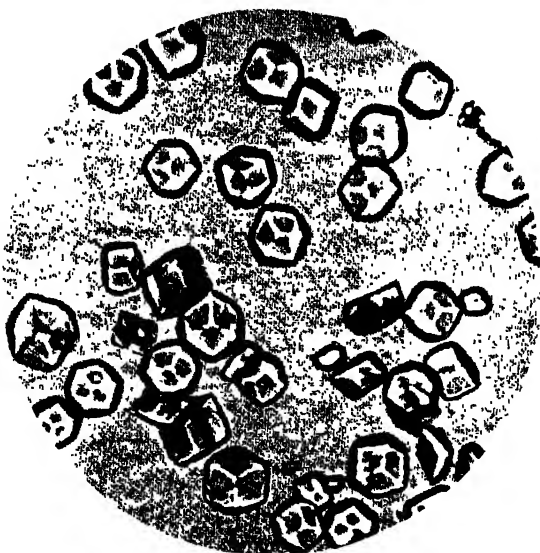
Temperature.	Half-life period
40°	6 months
30°	2 years
20°	10 "
10°	56 "
0°	377 "

Insulin does not dialyse readily through lodion membranes.

In solution, insulin is levo-rotatory, the degree of rotation depending on the reaction of the medium, thus:

Medium	Insulin strength	$[\alpha]$
0.002N. HCl	0.5%	40°
16N. acetic acid	0.5%	18° to 30°
13N. ammonia	0.5%	64°

Insulin has a characteristic absorption band lying between 2,500 and 2,900 $\mu$ , which has been ascribed to the cystine and tyrosine content. Ultra-violet light of various wave-lengths in the presence of oxygen inactivates insulin. Crowfoot (Nature, 1935, 135, 591) by X-ray photographs of single insulin crystals showed that they had simple rhombohedral cells with  $a = 44.3\text{\AA}$ , and  $a = 115^\circ$ . Their density was found to be 1.306. The crystal unit cell contains 1 mol. of insulin only and each molecule is surrounded by eight others, one each at 30 $\text{\AA}$ , above and below along the trigonal axis and six at 14 $\text{\AA}$ , along the edges of the primitive rhombohedron. Insulin



RHOMBOHEDRAL INSULIN CRYSTALS.

is adsorbed from water by fuller's earth, charcoal, kaolin, benzoic acid, salicylic acid and aluminium hydroxide.

**Chemical.**—Isoelectric or crystalline insulin can be converted into the hydrochloride or sulphate by dissolving in dilute hydrochloric or sulphuric acid and adding 10 vol. of acetone, when the salt separates as a flocculent white precipitate. Crystalline insulin exhibits the usual properties of a protein giving the biuret, Millon, Pauly, ninhydrin and xanthoproteic reactions. It does not contain phosphorus, however, and the tests for tryptophan and carbohydrate are negative. On heating, the crystals

turn brown at 215° and melt with decomposition at 233°. Apart from its zone of insolubility in aqueous solution from pH 4.5-6, insulin may be precipitated from solution by all the usual protein precipitants such as picric, tannic, flavanic, tungstic, trichloroacetic, phosphotungstic and Reinecke's acids, heavy metal hydroxides, etc. It may be salted out of acid solution completely by half saturation with neutral salts such as sodium chloride or ammonium sulphate, and in this respect more closely resembles a globulin than an ovalbumin. Attention has recently been directed to the precipitation of insulin in neutral solution by

basic substances such as histones, protamines or their degradation products, and by spermine and guanidine derivatives in attempts to produce complexes having more prolonged hypoglycæmic action.

The nitrogen and sulphur contents of crystalline insulin are variously given as 14.4–15.4% and 3.15–3.44%, respectively. Miller and du Vigneaud (J. Biol. Chem. 1937, **118**, 101) accounted for 95% of the sulphur as present in cystine when the hormone was hydrolysed by a mixture of formic and hydrochloric acids, while previously with ordinary hydrochloric acid hydrolysis it had been possible thus to identify only three-fourths of the total sulphur. Sullivan and Hess (*ibid.* 1939, **130**, 745) showed that recrystallisation of insulin from an ammonium acetate–pyridine buffer, while leaving the total sulphur content of the compound unchanged, affects a part of the cystine components in such a way as to lead to losses of sulphur in volatile form during hydrochloric but not hydrochloric–formic acid hydrolysis. Insulin recrystallised from a phosphate buffer showed no such evidence of labile cystine. No difference could be detected in the physiological assay value of the two products. Scott and Fisher (Biochem. J. 1935, **29**, 1048) found 0.52% of zinc in crystalline insulin, corresponding to 3 atoms of zinc per mol., assuming a molecular weight of about 37,000. Cohn *et al.* (J. Amer. Chem. Soc. 1941, **63**, 17) have used radioactive zinc to prepare insulin crystals so that analysis of zinc content could be carried out with reasonable accuracy on 0.2 g. After repeated equilibrations with conductivity water at reactions between  $p_H$  5 and 6.4, which would be expected to remove occluded zinc salts, a zinc content of about 0.3% corresponding to 2 zinc atoms per mol. was obtained even from crystals containing initially 0.6% zinc. Sahyun (J. Biol. Chem. 1941, **138**, 487) has, however, described a crystalline insulin with a zinc content of only 0.15%.

When insulin is heated in  $N/10$  HCl at  $100^\circ$ , a flocculent inactive precipitate forms which is soluble in dilute alkali at  $p_H$  11 and then regains its solubility in acid and also 80% of its activity.

Inactivation of insulin is brought about by  $HCHO$ , strong acids and alkalis, dilute  $HNO_3$ ,  $N/2$   $NH_4OH$ ,  $N/10$   $NaOH$ , acetic anhydride, 0.75*N*. HCl in 75%  $EtOH$ , cysteine, glutathione, thioglycolic and thioacetic acids,  $I_2$ ,  $H_2O_2$ ,  $Na_2SO_3$ ,  $K_2Fe(CN)_6$ ,  $H_2S$ ,  $H_2S_2$ , diazomethane, Na and Mg amalgams, Mel, leuco-Methylene Blue, hydrocyanic acid, ketene, ascorbic acid and quinol. These reagents may bring about inactivation by either: (1) reduction of the disulphide groups; (2) esterification or acetylation of the amino-, imino- or phenolic hydroxy-groups; (3) hydrolysis of peptide bonds; or (4) destruction of amino-groups, e.g. by  $HNO_3$ . Reduction by specific reagents of  $-S-S-$  groups, as in cystine and glutathione, irreversibly inactivates the hormone and in proportion as  $SH$  groups are set free, although the degree of inactivation increases much more rapidly than that of reduction. The reduced insulin has also lost the characteristic heat-precipitation reaction. Insulin may be acetylated with acetic anhydride in the cold

(Freudenberg *et al.*, Z. physiol. Chem. 1928, **175**, 1; 1932, **213**, 241), producing an inactive substance which may regain a large part of its activity on hydrolysis with dilute alkali. More recently, Stern and White (J. Biol. Chem. 1937–38, **122**, 371) have shown that the interaction of ketene and insulin produces acetylation of the amino-groups only, with no inactivation if the time of contact is short. After this, the phenolic hydroxy-groups are acetylated with loss of activity. Carr *et al.* (*ibid.* 1929, **23**, 1010) found that insulin became inactive when allowed to stand in acidified alcohol for several hours and was partially reactivated by dilute alkali. Inactivation also occurs with other solvents such as acetone in the presence of hydrochloric acid so that the process may be due to a reversible intramolecular rearrangement (Scott and Fisher, *ibid.* 1935, **29**, 1050) rather than to esterification. Hydrolysis of peptide bonds by acids or alkalis leads to irreversible inactivation accompanied by a decrease in cystine or amino-nitrogen content or both. Reversible inactivation is generally produced by reactions involving a blocking of the amino- or phenolic groups. The hypoglycæmic activity of insulin is thus apparently associated with certain dithio-, phenolic and probably amino-groups which are, however, found in most proteins. The activity is either a property of the molecule as a whole or is due to some labile unit which has hitherto escaped detection.

#### ENZYME ACTION.

Irreversible inactivation is produced by pepsin, trypsin and papain, but not by trypsin-free crepsin, non-activated kinase-free trypsin, aminopolypeptidases, dipeptidase, protaminases or carboxypolypeptidases. Any proteolytic or other degradation with a view to obtaining a smaller molecule with the same physiological actions has always resulted in less activity.

Harrington and Neuberger (*ibid.* 1936, **30**, 809), from results of electrometric titrations in aqueous and 80% alcohol solutions, deduce that insulin has an acid-binding capacity of  $43 \pm 2$  groups per mol. and a base-binding capacity of 60–70 groups per mol.

Insulin has been found to have a molecular weight of 35,000 and 37,000 by ultra-centrifugal and X-ray measurements respectively with a spherical molecule of the ovalbumin type.

The following table, by du Vigneaud (Cold Spring Harbor Monographs, 1938, Proteins, p. 279) of the distribution of aminoacids and other constituents is based on Bergman's theory of the presence of 288 mol. of aminoacid in the Svedberg unit of molecular weight 35,100.

Wrinch (Proc. Roy. Soc. 1937, A, **160**, 59; **161**, 505) in her cyclol theory suggested that the arrangement of these 288 residues in a closed cage molecule in the form of a truncated tetrahedron may be the appropriate structure for globular-type proteins like insulin, pepsin and egg albumin of molecular weight 35,000.

#### PHYSIOLOGICAL ACTION.

Insulin when injected lowers the blood sugar and, if the dose is large, may cause hypoglycæmic coma, convulsions and death. Intra-



Amino acid	Per cent amino acid residue		Molecules amino acid residue		Molecules calculated at 200 x 36
	Found	Calculated	Found	Calculated	
Lysine . . . . .	1.98	—	5.4	6	21 x 3 <sup>1</sup>
Arginine . . . . .	2.88	2.66	6.5	6	21 x 3 <sup>1</sup>
Histidine . . . . .	7.10	7.0	18.2	18	21 x 3 <sup>1</sup>
Tyrosine . . . . .	11.00	11.2	23.6	24	21 x 3 <sup>1</sup>
Cystine . . . . .	10.70	10.5	36.6	36	21 x 3 <sup>1</sup>
Glutamic acid . . . . .	26.30	26.4	71.6	—	21 x 3 <sup>1</sup>
Leucine . . . . .	25.90	23.2	80.4	—	21 x 3 <sup>1</sup>
Phenylalanine . . . . .	1.02	—	—	—	—
Proline . . . . .	10.02	—	—	—	—
Total accounted for . . . . .	85.862	83.16	242.3	234	—
Theoretical . . . . .	—	100.00	—	288	—

Constituent	Per cent		Molecules or groups		Molecules calculated as
	Found	Calculated	Found	Calculated	
Zinc . . . . .	0.52	0.56	2.8	3	20 x 3 <sup>1</sup>
Amide amino . . . . .	1.55	1.64	31	36	21 x 3 <sup>1</sup>
Sulphur . . . . .	3.2	3.28	35	36	21 x 3 <sup>1</sup>

venous injection produces the quickest response, and then subcutaneous, with intrathecal and subarachnoid the slowest. Although depression of blood sugar continues for several hours after intravenous injection, yet only 10% of the insulin remains in the blood after 50 minutes. For small doses in rabbits ( $\frac{1}{10}$ – $\frac{1}{2}$  U. per kg. body weight) the ratio dose/fall in blood sugar is logarithmic. Mice show little response at 18° but go into convulsions at 30°. The speed of action of insulin is dependent on the metabolic rate of the animal itself. Frogs react very slowly to doses of insulin. Insulin produces hypoglycaemia but no convulsions in the fowl. In man symptoms include hunger, fatigue, mental distress and delirium, and in cats salivation. Decreases in sugar of lymph and cerebrospinal fluid are also recorded. Insulin secretion occurs early in fetal life. Injection of insulin causes increases in acidity and chloride content of gastric juice in normal humans. Briggs *et al.* (J. Biol. Chem. 1923, **58**, 721) showed that insulin caused a decrease in concentration of blood-phosphorus and -potassium in animals, and Kay and Robison (Biochem. J. 1924, **18**, 1139) conclude that insulin brings about synthesis of esters of phosphoric acid in the corpuscles from the blood-glucose and inorganic phosphate. The blood of depancreatized animals contains 10–20 times as much acetaldehyde as normals and injections of insulin restore it to normal. Insulin counteracts adrenaline hyperglycaemia and simultaneous injections of insulin and adrenaline may produce no change in blood sugar. Bilaterally adrenalectomised animals are hypersensitive to insulin. Burn (J. Physiol. 1923, **57**, 318) found that pituitrin reduced adrenaline hyperglycaemia, but found an unexpected antagonism to insulin action by pituitrin. Burn and Marks (*ibid.* 1925, **60**, 131) found that thyroidectomy greatly increased the sensitivity

of animals to insulin. Insulin injection provokes a fall in body temperature. Houssay (New England J. Med. 1936, **214**, 961) found that diabetic symptoms following pancreatectomy were considerably ameliorated by hypophysectomy performed either before or after the removal of the pancreas. Young (Lancet, 1937, ii, 372) has found that injection of an anterior pituitary diabetogenic extract into dogs produces a condition simulating human diabetes, and further (Marks and Young, *ibid.* 1940, i, 493), that a "pancreatropic" extract prepared in another way from the same gland produced on injection an increase in the insulin content of rat pancreas. The exact rôle of insulin in carbohydrate metabolism is still obscure though a specific *in vivo* effect has been described by Krebs *et al.* (Biochem. J. 1938, **32**, 913) where the oxidation of citric acid by pigeon breast muscle is catalytically increased by insulin.

#### ADMINISTRATION OF INSULIN.

Insulin is usually administered in solution as the hydrochloride by subcutaneous injection. Intravenous or other parenteral injections, however, produce a blood-sugar-lowering effect. The requirements vary widely in different cases of diabetes and normally range from 5 to 100 units per person administered daily in 2–3 injections. Attempts made to obtain insulin preparations which could be given by mouth or as injections have not proved successful. Since insulin is destroyed by proteolytic enzymes, oral administration must be designed to protect it against the digestive action of pepsin and trypsin. In general large amounts of insulin mixed with alkali-, oil-, saponin- or trypsin-inhibiting substances have some slight effect when given orally, but this method of administration remains uncertain. Ointments of insulin and lanoline

have little effect on an intact skin, whereas a recently abraded skin allows appreciable absorption to take place. Insulin may be applied to the mucous surface of nose and mouth with slight action. Administration by the oral route, by injection or by endonasal application requires large amounts of insulin and does not permit accurate quantitative dosage.

Attempts have been made to prolong the action of insulin by retarding its absorption when injected (1) as an oil suspension or emulsion, (2) with a vasoconstrictor substance, and (3) as an insulin compound sparingly soluble in body fluids. The last has proved very successful. Hagedorn *et al.* (J. Amer. Med. Assoc. 1936, **106**, 177) showed that insulin may be combined with some basic group so that the compound may have its isoelectric point or zone of insolubility nearer to the reaction of tissue fluids than that of insulin itself. Kyrin, histones, globins and protamines were tried but only the compounds of insulin and protamines were found to have sufficiently low solubilities at  $pH$  7. In particular the compound of insulin with the protamine derived from rainbow trout, *Salmo irideus*, was found to have the very low solubility of  $10^{-6}$  in water at  $pH$  7.3. The amount of protamine combining with insulin is about 1:10. Injections of the insulin-protamine suspension have a considerably prolonged action when compared with insulin hydrochloride. Scott and Fisher (J. Pharm. Exp. Ther. 1936, **58**, 78) further showed that when a small amount of zinc (1 mg. per 500 units of insulin) is added to an insulin solution prior to the addition of protamine, the hypoglycaemic action of the resulting suspension is even more prolonged than that of protamine-insulin without zinc. This protamine-zinc-insulin suspension is now frequently administered in preference to insulin hydrochloride, since one single daily injection of the suspension each morning may control glycaemia and glycosuria where 2 or 3 injections of hydrochloride were previously required.

Parkes and Young (J. Endocrinol. 1939, **1**, 108) have reported that the implantation of pellets of solid crystalline insulin has a prolonged action. Insulin has recently been used with success in the "shock" treatment of catatonic stupor and schizophrenia in which a coma-producing dose is given (Dussik and Sakel, Z. ges. Neurol. u. Psychiat. 1936, **155**, 351).

#### STANDARDISATION.

Despite what is known of the chemical nature of insulin no chemical property or properties can be used as a true criterion of potency. Even its crystalline form is not necessarily a criterion of homogeneity, since crystals have been obtained of potency 70% of the standard. In 1935 the League of Nations Health Organisation adopted as standard a sample of insulin recrystallised 10 times under the supervision of Dr. Scott at Toronto. To this pure insulin there has been attributed after numerous biological tests in different laboratories the value 22 units per mg. All insulin is assayed in terms of this standard which has been distributed to various centres throughout the world. All the methods of

assay are, therefore, biological. In the rabbit test the animals are divided into two groups, one injected with the standard and the other with the unknown. Some days later the test is repeated with the same animals but with the groups reversed. The reductions of blood sugar in the rabbits injected with the standard insulin are then compared with the reductions produced by the sample of unknown potency. In the mouse test, carried out in a thermostat at 38°, the number of mice sent into convulsions by a certain dose of the solution to be tested is compared with the number convulsed by varying doses of the standard solution. The assay of a suspension of protamine-zinc-insulin made from a previously standardised insulin solution by the addition of zinc and protamine is carried out on rabbits against either a standard protamine-zinc insulin-suspension or against an ordinary standard insulin hydrochloride solution, the shape of the prolonged-action curve falling within certain prescribed limits.

#### INTERATOMIC DISTANCES. — T. F. D.

The distances between the atoms in a molecule may be determined by two entirely different methods, generally known as (a) the spectroscopic method, and (b) the diffraction method. Each of these general methods may be subdivided. The first of the spectroscopic methods is based on the evaluation of the moments of inertia of the molecule from the fine structure in the molecular spectrum due to the rotation of the molecule; the second is based on an empirical relation between the interatomic distance (or bond) in question and its associated force constant, the latter being deduced from the vibrational frequencies in the spectrum. In this article these two spectroscopic methods will be denoted by the respective symbols  $S_1$  and  $S_2$ . The first of the diffraction methods is based on the theory of the diffraction of X-rays by a crystal lattice; the second is based on the theory of the diffraction of electrons by a gas. It is possible also to obtain interatomic distances by the diffraction of X-rays in gases and the diffraction of electrons by crystals, but the accuracy in each case is very low and these methods need not be considered. The two diffraction methods will be denoted by  $D_x$  and  $D_k$  according as X-rays or electrons are being diffracted.

The  $S_1$  method is applicable when the individual rotation lines of the spectrum can be resolved, and is by far the most accurate of all the four methods, the error being generally less than 0.001 Å. Unfortunately this method has not a wide range of applicability, for the rotation lines become more difficult to resolve as the size of the molecule increases, since the spacings between them depend on reciprocals of the moments of inertia of the molecule. Moreover it is obviously not possible to determine all the interatomic distances and angles in a complex molecule from a knowledge of the three moments of inertia. This last difficulty may be overcome to some extent by using different isotopic forms of the same molecule and by making assumptions regarding certain of the interatomic distances and interbond angles well established from other molecules.

H (0.30)	Li		Be		B (0.88)	
	${}^1\text{H}_2$ $S_1$	${}^2\text{H}_2$ $S_1$	$\text{Li}_2$ $S_1$		$\text{B}_2\text{H}_6$ $D_{2h}$	$\text{B}_2\text{H}_6$ $S_1$
Li (0.30)	1.596 $\text{Li}_2\text{H}$ $S_1$					
Be (0.30)	1.343 $\text{Be}_2\text{H}$ $S_1$					
B (0.88)	1.231 $\text{B}_2\text{H}$ $S_1$	1.27 $\text{B}_2\text{H}_6$ $D_{2h}$				1.594 $\text{B}_2\text{H}_6$ $S_1$
C (0.77)	1.120 $\text{C}_2\text{H}$ $S_1$	1.093 $\text{CH}_4$ $S_1$	1.04 $\text{CH}_2\text{O}$ $S_1$		1.56 $\text{B}(\text{CH}_3)_3$ $D_{2h}$	
N (0.70)	1.038 $\text{N}_2\text{H}$ $S_1$	1.016 $\text{NH}_3$ $S_1$			1.44 $\text{B}_3\text{N}_3\text{H}_6$ $D_{2h}$	1.281 $\text{BN}$ $S_1$
O (0.66)	0.971 $\text{O}_2\text{H}$ $S_1$	0.969 $\text{H}_2\text{O}$ $S_1$		1.331 $\text{BeO}$ $S_1$	1.205 $\text{BO}$ $S_1$	
F (0.64)	0.917 $\text{HF}$ $S_1$			1.362 $\text{BeF}$ $S_1$	1.309 $\text{BF}$ $S_1$	1.29 $\text{BF}_3$ $S_1$
Na (0.30)	1.888 $\text{Na}_2\text{H}$ $S_1$	1.887 $\text{Na}_2\text{H}$ $S_1$				
Mg (0.30)	1.731 $\text{Mg}_2\text{H}$ $S_1$	1.730 $\text{Mg}_2\text{H}$ $S_1$				
Al (0.30)	1.646 $\text{Al}_2\text{H}$ $S_1$	1.646 $\text{Al}_2\text{H}$ $S_1$			2.14 $\text{AlB}_3\text{H}_2$ $D_{2h}$	
Si (1.17)	1.521 $\text{Si}_2\text{H}$ $S_1$	1.46 $\text{Si}_2\text{H}_6$ $D_{2h}$				
P (1.10)	1.431 $\text{P}_2\text{H}$ $S_1$	1.46 $\text{PH}_3$ $S_1$				
S (1.04)	1.35 $\text{H}_2\text{S}$ $S_1$					
Cl (0.99)	1.275 $\text{H}_3\text{S}^+\text{Cl}$ $S_1$	1.275 $2\text{H}_3\text{S}^+\text{Cl}$ $S_1$			1.73 $\text{BCl}_3$ $D_{2h}$	1.716 $\text{BCl}_3$ $S_1$

C  
177

C (0.77)	N (0.70)									
	1.542 Diamond D <sub>C</sub>	1.55 C <sub>2</sub> H <sub>6</sub> D <sub>r</sub>	1.39 C <sub>6</sub> H <sub>6</sub> D <sub>r</sub>	1.33 C <sub>3</sub> H <sub>4</sub> S <sub>1</sub>	1.312 C <sub>2</sub> S <sub>1</sub>	1.204 C <sub>2</sub> H <sub>2</sub> S <sub>1</sub>	1.46 MeC <sub>2</sub> CH S <sub>1</sub>	1.52 Glycine D <sub>r</sub>		
N (0.70)	1.172 CN S <sub>1</sub>	1.15 HCN S <sub>1</sub>	1.13 CICN D <sub>r</sub>	1.47 N(CH <sub>3</sub> ) <sub>3</sub> D <sub>r</sub>	1.39 Glycine D <sub>r</sub>	1.37 Urea D <sub>r</sub>	1.47 CH <sub>3</sub> N <sub>3</sub> D <sub>r</sub>	1.47 C(NO <sub>2</sub> ) <sub>4</sub> D <sub>r</sub>	1.47 N <sub>2</sub> H <sub>4</sub> D <sub>r</sub>	1.6-1.7 N <sub>2</sub> O <sub>4</sub> D <sub>r</sub>
	1.128 CO S <sub>1</sub>	1.16 CO <sub>2</sub> S <sub>1</sub>	1.20 CH <sub>3</sub> O S <sub>1</sub>	1.42 (CH <sub>3</sub> ) <sub>2</sub> O D <sub>r</sub>	1.425 CH <sub>3</sub> OH S <sub>1</sub>	1.26 Glycine D <sub>r</sub>	1.25 Urea D <sub>r</sub>	1.15 NO S <sub>1</sub>	1.13 CH <sub>3</sub> N <sub>2</sub> D <sub>r</sub>	1.18 N <sub>2</sub> O <sub>4</sub> D <sub>r</sub>
O (0.66)	1.39 CH <sub>3</sub> F S <sub>1</sub>	1.42 CH <sub>3</sub> F D <sub>r</sub>	1.36 CF <sub>4</sub> D <sub>r</sub>	1.34 C <sub>2</sub> H <sub>5</sub> F D <sub>r</sub>					1.208 O <sub>2</sub> S <sub>1</sub>	1.48 H <sub>2</sub> O <sub>2</sub> D <sub>r</sub>
F (0.64)									1.41 F <sub>2</sub> O D <sub>r</sub>	
Na										
Mg										
Al	2.05 Al <sub>2</sub> (CH <sub>3</sub> ) <sub>6</sub> D <sub>r</sub>								1.618 AlO S <sub>1</sub>	
Si (1.17)	1.93 Si(CH <sub>3</sub> ) <sub>4</sub> D <sub>r</sub>								1.510 SiO S <sub>1</sub>	
P (1.10)	1.87 P(CH <sub>3</sub> ) <sub>3</sub> D <sub>r</sub>								1.447 PO S <sub>1</sub>	1.56 POF <sub>3</sub> D <sub>r</sub>
S (1.04)	1.52 CS <sub>2</sub> S <sub>1</sub>	1.54 CS <sub>2</sub> D <sub>r</sub>		1.82 S(CH <sub>3</sub> ) <sub>2</sub> D <sub>r</sub>					1.494 SO S <sub>1</sub>	1.43 SO <sub>2</sub> D <sub>r</sub>
Cl (0.99)	1.69 CH <sub>3</sub> Cl S <sub>1</sub>	1.77 CH <sub>3</sub> Cl D <sub>r</sub>	1.75 CCl <sub>4</sub> D <sub>r</sub>	1.68 HC <sub>2</sub> Cl D <sub>r</sub>				1.95 NOCl D <sub>r</sub>	1.68 Cl <sub>2</sub> O D <sub>r</sub>	1.53 ClO <sub>2</sub> D <sub>r</sub>
										1.45 SOCl <sub>2</sub> D <sub>r</sub>

F (0.64)		Na (0.64)		Mg		Al	
F (0.64)	1.415 F <sub>2</sub> D <sub>1</sub>						
Na		3.079 Na <sub>2</sub> S <sub>1</sub>					
Mg							
Al						2.02 Al <sub>2</sub> (CH <sub>3</sub> ) <sub>6</sub> D <sub>1</sub>	
Si	1.54 SiF <sub>4</sub> D <sub>1</sub>						
P	1.52 PF <sub>3</sub> D <sub>1</sub>						
S	1.56 SO <sub>2</sub> F <sub>2</sub> D <sub>1</sub>						
Cl	1.64 ClF D <sub>1</sub>	2.51 NaCl D <sub>1</sub>				2.14 AlCl S <sub>1</sub>	

Si (1.17)		P (1.10)		S (1.04)		Cl (0.99)	
Si (1.17)	2.32 Si <sub>2</sub> H <sub>6</sub> D <sub>1</sub>						
P		1.895 P <sub>2</sub> S <sub>1</sub>	2.21 P <sub>4</sub> D <sub>1</sub>	3.0 P <sub>2</sub> O <sub>6</sub> D <sub>1</sub>	2.84 POCl <sub>3</sub> D <sub>1</sub>		
S		1.85 PSF <sub>3</sub> D <sub>1</sub>	1.94 PSCl <sub>3</sub> D <sub>1</sub>	1.89 S <sub>2</sub> S <sub>1</sub>	1.92 S <sub>2</sub> D <sub>1</sub>	2.08 S <sub>2</sub> D <sub>1</sub>	2.05 S <sub>2</sub> H <sub>2</sub> D <sub>1</sub>
Cl	2.02 SiCl <sub>4</sub> D <sub>1</sub>	2.00 PCl <sub>3</sub> D <sub>1</sub>	2.2 PCl <sub>5</sub> D <sub>1</sub>	2.00 SCl <sub>2</sub> D <sub>1</sub>	2.07 SOCl <sub>2</sub> D <sub>1</sub>	1.99 SO <sub>2</sub> Cl <sub>2</sub> D <sub>1</sub>	1.989 Cl <sub>2</sub> S <sub>1</sub>

The  $S_2$  method is only applied when the rotational structure of the spectrum is smeared out, either because the moments of inertia of the molecule are very large (around  $100 \times 10^{-40}$  g.-cm.<sup>2</sup>) or because the molecules are not in the gaseous state. By using only the vibrational structure of the spectrum it is possible in many cases to deduce the values of the force constants which characterise the resistance of the various bonds in the molecule to stretching. Denoting the force constant of a bond by  $k_r$  then the restoring force brought into play when the bond is stretched by an amount  $x$  from its equilibrium value is  $k_r x$ , and it has been found that  $k_r$  can be related to the equilibrium bond distance,  $r_e$ , by various empirical formulae. The constants in these formulae depend on the positions of the two atoms in the periodic table and are determined from molecules investigated by the  $S_1$  method. The formulae can then be applied to more complex molecules to estimate interatomic distances with an error varying between 0.01 and 0.05 Å. Although this method does not at present possess the accuracy of the other spectroscopic method, it has a potentially much wider field of application.

The  $D_x$  method depends on the fact that a crystal acts towards a beam of X-rays as a three-dimensional reflection grating and that the resulting diffraction pattern can be computed from the relative positions of the atoms in the lattice and a knowledge of their scattering powers. It is not possible to compute the positions of the atoms in the lattice directly from the X-ray pattern although recent developments have made it possible to locate the heavier atoms in a structure. The probable errors in this method lie between 0.01 and 0.05 Å, except in cases where the interatomic distance is determined directly by the size of the unit cell (*e.g.* diamond) when it may be reliable to 0.001 Å.

The  $D_E$  method suffers from the same disadvantages as the  $D_x$  method, in that the interatomic distances cannot be deduced directly from the diffraction pattern of the electrons after passing through the vapour of the compound. The patterns to be expected from various models of the molecule can be computed and by trial and error a model is arrived at which gives the correct diffraction pattern. The accuracy of this method is much the same as that of the X-ray method, an average figure for the error being 0.03 Å. It should be added that both the diffraction methods are practically useless in •locating hydrogen atoms.

In the preceding chart have been collected most of the interatomic distances for atoms in the first two periods for which reliable values are now available. Below each distance is given the molecule in which this particular distance was found, and below that a symbol (defined above) indicating the method employed in the determination. In parentheses below each atom is given the Pauling-Huggins covalent radius for that atom. According to Pauling (L. Pauling "The Nature of the Chemical Bond," 1st ed., Cornell University Press, 1939, p. 153) any single bond interatomic distance can be predicted by taking the sum of the relevant covalent radii; for a double bond this sum should be re-

duced by the factor 0.87, and for a triple bond, by the factor 0.78. Interatomic distances which lie between single and double bond, or double and triple bond distances are then taken to indicate the existence of two or more resonating structures for the molecule. Thus the C—C distance in benzene is 1.39 Å., compared with a single bond distance of 1.54 Å. and a double bond distance of 1.33 Å., indicating that resonance exists in benzene. However, the Pauling-Huggins radii are not reliable enough to be applied generally in this way and modifications have recently been suggested by Schomaker and Stevenson to take account of the electronegativity of the atoms.

The distances given in the chart were compiled from the following sources, which should be consulted for further details, and for interatomic distances between the heavier atoms:

*Spectroscopic*—G. Herzberg, "Molecular Spectra of Diatomic Molecules," Prentice-Hall, 1939; Articles on Spectroscopy by G. B. B. M. Sutherland (Chem. Soc. Annual Rep. for 1936 and 1938); Papers by Herzberg, Douglas and others on  $B_2$ ,  $BH$ ,  $BCl_3$  and  $P_2$  (Canad. J. Res. 1940 and 1941); N. R. Davidson, J. A. C. Hugill, H. A. Skinner and L. E. Sutton (Trans. Faraday Soc. 1940, 36, 1212) for  $Al-Al$  and  $Al-C$  distances.

*Electron Diffraction*.—Review article by L. R. Maxwell (J. Opt. Soc. Amer. 1940, 30, 375); V. Schomaker and D. P. Stevenson, on some revised values of the covalent radii (J. Amer. Chem. Soc. 1941, 63, 37).

*X-ray and General*.—L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, 1939; R. B. Corey, on interatomic distances in proteins (Chem. Reviews, 1940, 26, 227). G.B.B.M.S.

**INTERFACIAL ANGLES.** The contact angle  $\theta$  (fig. 1) between a liquid and a solid surface is defined as the angle, measured in the liquid, at which the liquid rests in contact with

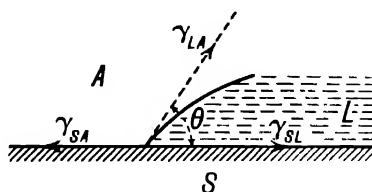


FIG. 1.

the solid. By resolving the surface tensions parallel to the solid surface, it is seen that

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta \quad (1)$$

$\gamma_{SA}$ ,  $\gamma_{SL}$ ,  $\gamma_{LA}$ , being the solid-air, solid-liquid, and liquid-air tensions. If (1) is combined with the well-known equation of Dupré, which gives a necessary relation between the surface tensions and  $W_{SL}$ , the "work of adhesion" between solid and liquid, or the work required per square centimetre to separate solid from liquid, against the adhesive forces between them, we have

$$W_{SL} = \gamma_{LA} + \gamma_{SA} - \gamma_{SL} \quad (2)$$

We also have what is now usually known as Young's equation (3), discovered by Thomas Young in 1805,

$$W_{SL} = \gamma_{LA}(1 + \cos \theta). \quad (3)$$

This equation shows what are the essential forces which determine the magnitude of the contact angle. If the work of adhesion,  $W_{SL}$ , equals (or exceeds)  $2\gamma_{LA}$ , which is the work required to break a column of the liquid of 1 sq. cm. cross-section, or the "work of cohesion" of the liquid, the contact angle  $\theta$  must be zero. The angle will be  $90^\circ$  if the adhesion of the liquid to the solid is just half that of the liquid for itself; and if the adhesion between liquid and solid could be diminished to zero, the contact angle would become  $180^\circ$ ; this is not, however, possible.

The term "wetting," of a solid by a liquid, which has always been recognised as intimately connected with the contact angle, is now usually defined as follows: if the contact angle is zero, the wetting is complete or perfect; if the contact angle is finite, wetting is incomplete or imperfect. More loosely, surfaces are sometimes said to be unwettable, or to repel water, if the contact angle is large, greater than  $90^\circ$ ; there is always, however, some degree of adhesion between any solid and any liquid in contact with it. If wetting is perfect, the liquid spreads easily in a film over the whole surface; if wetting is imperfect, the liquid gathers itself into separate drops and for a given quantity of liquid the area of contact of the drops with the solid is smaller the greater the contact angle and the poorer the wetting.

Contact angles much greater than  $90^\circ$  are rare; paraffin wax and water form an angle of about  $105^\circ$ , which is about the largest contact angle ever found between an organic substance and water. This large angle is due to the adhesion between water and the hydrocarbon groups forming the surface of the wax being rather small, while the surface tension of water is unusually large, and consequently the adhesion of the water to the wax is very much less than the cohesion of the water. Liquid metals form a very high contact angle with glass or silica; mercury ordinarily rests at about  $140^\circ$ , though the angle depends a good deal on the condition of the glass, and may occasionally become acute if the glass be carefully baked out under high vacuum. These high angles are due to the exceptionally high surface tension and cohesion of metals; their surface tension is usually several hundred dynes per cm., and may exceed 1,000 dynes per cm., so that the cohesion of metals is much higher than their adhesion to almost all surfaces, except to other clean metals.

Contact angles are extremely sensitive to the state of the solid surface. It is possible, by depositing a layer of oleic acid on clean glass, which is perfectly wetted by water, to reduce the adhesion so much that the contact angle rises to about  $90^\circ$ , and the surface is thus changed from a strongly hydrophilic to a hydrophobic surface. Sometimes small amounts of water, or other liquid, can soak into a surface which forms a large contact angle and considerably reduce the angle.

Most solids and liquids show a phenomenon called hysteresis of the contact angle, which may have any value between two extremes: a liquid advancing over a solid generally gives a larger angle than the same liquid receding from a previously wetted part of the same surface. Hysteresis, i.e. the difference between the advancing and the receding angles of contact, is often very large with water, amounting sometimes to  $60^\circ$  or more, the liquid being able to rest on the solid at any angle between the two extremes of the advancing and the receding angle. Ablett (Phil. Mag. 1923, [vi], 46, 244) found that the amount of hysteresis depends on the speed of the advancing or receding motion, but usually the angle at which advancing motion first begins is considerably greater than that at which the liquid can be induced to start receding from a wetted surface. The appearance is as if the edge of the liquid tended to adhere to the old surface. While hysteresis is greatest with water, most liquids show it to some extent; some writers claim that its amount can be substantially reduced if the solid surface is very thoroughly cleaned. Its practical importance is considerable, but there is not yet universal agreement as to its cause, which may indeed vary in different cases. Very small amounts of grease might account for the hysteresis with water and such hydrophilic surfaces as glass and some minerals, the grease being displaced after the water covers the surface; alternatively some of the liquid may soak into, or be adsorbed on to, the solid, increasing its attraction for the liquid after wetting. Langmuir has suggested that the molecules of a very thin film of grease may actually be overturned by contact with the water so that their hydrophilic terminal groups are outwards, and the attraction for water is increased. After drying, the molecules are supposed to revert to their normal position, with the hydrophilic terminal groups downwards, and thus the attraction for water decreases because the surface consists of hydrocarbon groups. Whatever the precise cause of hysteresis, it is clear that it is the result of a variation in the amount of adhesion of the surface for the liquid, according to whether or not it is being wetted by the liquid.

Methods of measuring contact angles are numerous. If the solid can be obtained in the form of a flat plate, or even a wire or a straight fibre, a good method is to fix the solid in a holder which can be set at any angle to the liquid surface, and to dip it into the liquid and adjust the angle until the surface of the liquid remains accurately horizontal right up to the point of contact with the solid. Then the angle between the liquid surface and the solid is the contact angle. It is necessary to provide means of raising and lowering the solid in the water, to find the advancing and the receding angles; also, if the angle with clean water is required, means must be provided of cleaning the liquid surface, since the surface of water is very easily contaminated by grease, with lowering of the surface tension and of the contact angle. Other methods depend on observing the direction of a ray of light reflected from the liquid and the solid surface very near to the line of contact between

them. These methods are accurate to a very few degrees, which is usually sufficient, since the contact angle of a solid surface generally varies by this amount in different parts. Direct observation under the microscope of the angle at which solid and liquid surfaces meet is sometimes possible, and reasonably accurate; or a magnified image may be projected on a screen and the angle measured with a protractor. Another method is to measure the height to which the liquid rises in a capillary tube of known radius; if the surface tension of the liquid is known, the contact angle between the liquid and the tube can be calculated from the formula

$$h = \frac{2\gamma_{LA} \cos \theta}{gr(D-d)}$$

$h$  is the height of rise,  $r$  the radius of the tube,  $D$  the density of the liquid and  $d$  that of the air. Alternatively the pressure required just to prevent the liquid from entering a capillary tube may be measured. This is the foundation of Bartell and Osterhof's method for finding the contact angle of a substance available only in powder form: a highly compressed plug is made of the powder, liquid is put in contact with the powder at one side and the pressure required to balance its tendency to penetrate into the plug is measured. A difficulty in this method is the determination of the "radius" of the capillary tube equivalent to the plug of powder; but at present it is almost the only method available for a quantitative determination of the contact angle of a fine powder against a liquid.

The practical importance of contact angles and wetting is very widespread. Sometimes the best possible wetting is desirable, sometimes the least possible. The precise conditions to be attained vary slightly according to whether good *spreading* of the liquid over a large area of solid, or good *penetration* of the liquid into the pores of a porous solid or heap of powder is required; conversely, the prevention of spreading of a liquid over a solid surface, or hindering its penetration into pores, are not exactly similar problems.

Good spreading over the largest possible area of solid surface is required for all insecticide and disinfectant sprays and dips, so that a small quantity of liquid shall cover the largest possible area of the plant, animal or other surface to be treated. The windows of gas-masks, goggles or other transparent windows where there is a warm, moist atmosphere on one side and a colder one on the other, mist up or "dim" after a time, often so badly that it becomes impossible to see through them, unless the moisture can be condensed in a continuous thin film instead of in separate droplets. In many types of chemical plant, such as gas absorption towers or film evaporators, where a rapid interchange of a substance between vapour and liquid is required, the liquid is made to trickle over a large area of solid surface so as to expose the largest possible area and the smallest possible thickness to the vapour. Unless the liquid spreads perfectly, wetting the solid everywhere, the area will be reduced and the thickness increased, so that exchange of gas between liquid and vapour,

or evaporation, is slower than it should be; very serious loss of efficiency may result if wetting is poor. In cases where the maximum spreading is required, the contact angle must have a minimum value; unless the receding angle is zero, the liquid will not remain spread even if mechanically forced to cover the whole surface; and for the liquid to spread itself without the expenditure of much energy and careful control of the direction at which the liquid impinges on the solid, the advancing angle also must be zero, a condition which is more difficult to attain.

Few surfaces give a zero contact angle with water for long, since minute traces of grease produce a finite angle even on such surfaces as glass, which do wet completely if absolutely clean. There are now many wetting agents available, water-soluble substances which often enormously improve the wetting. They operate either by diminishing the surface tension of the liquid, or by increasing its adhesion for the solid, sometimes in both ways. Inspection of equation (3) shows that  $\cos \theta$  is increased and therefore  $\theta$  is diminished, either by increasing  $\gamma_{SL}$  or by decreasing  $\gamma_{LA}$ . Most wetting agents have the general constitution  $\text{RX}$ ,  $\text{R}$  being a hydrocarbon group of considerable size, generally a long aliphatic chain, but sometimes an aromatic or aliphatic group,  $\text{X}$  is a strongly water-attracting group, and the variety of such end groups is now very great, the  $\text{COONa}$  group of soap being one of these. Alkyl sodium sulphates  $\text{ROSO}_3\text{Na}$ , many other sulphates or sulphonates, and amides variously substituted and generally sulphonated are common wetting agents. Some very successful modern wetting agents are polyphenols substituted with one or more alkyl chains and sulphonated. Other wetting agents are un-ionised substances such as polyglycerol esters or polyethylene oxides.

The decrease of surface tension is mainly due to the hydrocarbon part of the molecules; all substances containing long hydrocarbon chains tend to be adsorbed at the surface and to form a layer in which they usually lie flat in the surface; this reduces the field of attractive force at the surface, and consequently the surface tension. One hydrocarbon chain containing over six carbon atoms in a soluble compound can usually, at a sufficient concentration, reduce the surface tension of water to between 20 and 30 dynes per cm. instead of 73 for clean water, and very low concentrations of substances with twelve or more carbon atoms in an aliphatic chain achieve a similar decrease in surface tension. The great majority of wetting agents are powerful depressants of surface tension.

Whether the wetting agent actually increases the adhesion of the water to the solid depends on the constitution of the solid surface and on the end-group  $\text{X}$  of the molecule of the wetting agent; any increase in such adhesion will improve the wetting. An interesting, though not particularly important, phenomenon is shown by the salts of some quaternary bases with long aliphatic chains, such as cetyltrimethylammonium or cetylpyridinium hydroxide. In extremely dilute solution these long-chain cations are adsorbed on glass (which has a



negative electric charge when immersed in water) with their hydrophilic end-groups inwards and their hydrocarbon chains outwards; and the effect of washing clean glass with these dilute solutions is to reduce the adhesion and produce a contact angle of some magnitude, causing a greasy appearance on a previously clean surface. Increase in concentration reduces the surface tension so far that the contact angle again falls to zero. In general, it can be said that if a soluble substance contains groups which tend to combine with the material of the solid surface, or to dissolve it, wetting will be assisted as a result of increasing the adhesion of the liquid for the solid; but at present our knowledge of the adsorption of molecules at solid liquid surfaces is much less complete than that of the structure of films at air-water surfaces.

Good wetting of metals by oils is desirable in lubrication. There is usually little difficulty in obtaining a low or a zero contact angle between ordinary oils and metals, but it is often useful deliberately to increase the adhesion between them by adding fatty acids, the end groups of which attract and sometimes combine with the surface of the metal. This helps to prevent the layer of molecules in the liquid next to the solid from being easily rubbed off, and thus improves "boundary" lubrication, or lubrication under conditions such that the film of lubricant is reduced to molecular thickness. Glycerides (animal or vegetable oils) are better boundary lubricants than mineral oils, because they adhere more closely to the solid.

Perfect wetting of a metal by molten solder is essential for successful soldering or brazing. Molten solders will not spread on greasy or oxidised surfaces, but spread excellently on clean surfaces; hence the surface must first be thoroughly cleaned, and also protected by a suitable flux against surface oxidation during heating.

Good penetration of a liquid into the pores of a porous solid also requires good wetting, but here the quantity  $\gamma_{LA} \cos \theta$ , usually termed the "adhesion tension," should be a maximum, not merely the contact angle a minimum, as for simple spreading. Spreading on a smooth solid surface will not take place unless the contact angle is zero, but penetration into a capillary space will occur to some extent if the adhesion tension,  $\gamma_{LA} \cos \theta$ , is positive, i.e. if the advancing contact angle is less than  $90^\circ$ . Two important cases in industry are the "wetting-out" of textiles by water, a necessary preliminary to scouring, bleaching or dyeing operations, and the laying of dust by water, especially in mines. The cloth may be difficult to wet from natural causes, or because of the size used in weaving; coal dust and many stone dusts are also quite difficult to wet. Wetting agents are useful in both these cases, indeed often almost essential.

Good dispersion of a solid in a liquid requires good wetting. Here it is necessary for the adhesion between the liquid and solid to be sufficient for the liquid to spread over the whole solid surface, and the larger this adhesion, probably even in excess of that required to give zero contact angle, the less chance there will be of the solid particles adhering to each other and

settling out in lumps or hard masses which cannot be redistributed evenly through the liquid merely by stirring. Poor wetting of the pigment by the oil is a frequent cause of defects in paints. Here, suitable wetting agents have to act by increasing the adhesion of the solid to the liquid; the surface tension of paint media is usually not high.

There are some processes in which wetting must be reduced to the minimum possible amount, as in the flotation of minerals (*v. FLOTATION PROCESS*, Vol. V, 263*d*), and the showerproofing of textiles (*v. FINISHING TEXTILE FABRICS*, Vol. V, 193*d* 198*a*).

It has been suggested that condensers in steam engines could be made much more efficient if the steam could be condensed in the form of separate drops covering a small fraction only of the condensing surface. This is because the principal resistance to rapid conduction of heat seems to be the liquid film which is stagnant up to a small thickness on the condensing surface; if condensation could be made to occur so that this film did not form, a much increased rate of heat conduction and therefore of condensation could theoretically be achieved. Nagle, Drew *et al.* (*Trans. Amer. Inst. Chem. Eng.* 1933-34, 30, 217, 1935, 31, 593) have obtained some success in this field, but as yet the difficulties attendant on large-scale utilisation do not seem to be overcome.

The contact angle formed by the interface between two liquids, and a solid, is also of practical importance. It may be finite, or zero in one liquid and  $180^\circ$  in the other. In the latter case, a powdered solid will tend to pass wholly into the liquid in which the angle is zero and preferential wetting by this liquid may be said to be perfect. If the contact angle is finite, the powder will tend to remain at the surface between the liquids, just as a powder with a finite air-liquid-solid contact angle can float at the air-liquid surface. Powders thus retained at a liquid-liquid surface by surface forces help to stabilise emulsions of the two liquids, since the powder naturally hinders the contraction of the surface, which accompanies breaking of the emulsion by coalescence of the drops (*v. EMULSIONS AND EMULSIFICATION*, Vol. IV, 284*a*).

The action of soap and other similar detergents in removing grease is largely due to their

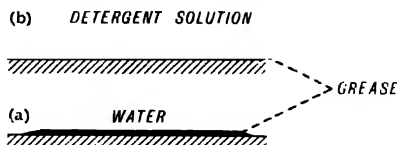


FIG. 2.

effect in changing the contact angle made by the surface between the grease and the water. Microscopic observation (Adam, *J. Soc. Dyers and Col.* 1937, 53, 124) has shown that, in water, grease on wool forms a thin film with practically zero contact angle in the grease (fig. 2, a). In dilute cetyl sodium sulphate solution, a very efficient detergent for wool, the angle changes

to 180° in the grease and zero in the water, and thus the grease becomes detached (Fig. 2, b) on very slight mechanical agitation.

The displacement of one liquid, such as oil, by another liquid such as water, from a porous sand is analogous to the penetration of a single liquid into a dry porous solid. It will occur if the (advancing) contact angle of the surface between the liquids is acute in that liquid which advances and displaces the other; for the most rapid displacement the adhesion tension of the water for the solid must exceed that of the oil by the largest possible amount. This property is probably of great importance in underground oil deposits.

Contact angles between two liquids and air, no solid being present, are important for the spreading of oils on water, which is used on a large scale in the control of malarial mosquitoes. The angle here is that in the oil, between its upper and lower surfaces, where they meet the water surface. To ensure spreading this contact angle must be zero; for this it is necessary that

$$\gamma_{WA} > \gamma_{OA} + \gamma_{OW} \quad (1)$$

$\gamma_{WA}$ ,  $\gamma_{OA}$ , are the surface tensions of the water and the oil, and  $\gamma_{OW}$  the interfacial tension between the oil and the water. It can easily be shown that (4) is equivalent to the condition that the work of adhesion of the oil to the water must exceed the work of cohesion of the oil for itself; the difference should preferably be as large as possible, to provide a margin of spreading power and give the greatest chance of spreading on slightly contaminated surface. The difference  $\gamma_{WA} - \gamma_{OA} - \gamma_{OW}$  is often called the "spreading coefficient"; it should be at least 16 dynes per cm. and preferably more. *Pure* mineral oils do not spread, and have a negative spreading coefficient; the sign can be reversed mainly by increasing the adhesion between oil and water, with quite small amounts of oil-soluble substances containing hydrophilic groups, among the most powerful of these are sulphonic acid groups. The oxidation products of unsaturated oils, formed by the action of air and light, also assist spreading. Most commercial oils have a positive spreading-coefficient. Initial high spreading-power is not, however, the only requirement, for the films of oil, once spread, are usually unstable and tend to break up into films of molecular thickness, probably one molecule thick and too thin to affect the larvae, the remainder of the oil collecting into small drops which form a finite contact angle and do not spread. The phenomena of break-up of spread oil-films are complex and not yet fully understood (cf. D. R. P. Murray, *Bull. Entomol. Res.* 1938, 29, 11; 1939, 30, 211).

For further information, and references to original papers, see Harvey, "Wetting and Detegency," Chemical Publishing Co., New York, 1937; and Adam, "The Physics and Chemistry of Surfaces," 3rd ed., Oxford, 1941, pp. 178-215, 413-414.

N. K. A.

**INUKAYA OIL** (Inugaya or Bébé oil) prepared by steaming and pressing the seed-kernels (which contain about 67% of the oil) of

the Japanese evergreen inukaya tree, *Cephalotaxus drupacea* Sieb. and Zucc. (Fam. Taxaceae).

The cold-expressed oil prepared in the laboratory by Tsujimoto (J. Coll. Eng. Tokyo, 1908, 4, 85; Chem. Rev. 1908, 5, 168) was pale-yellow in colour with a faint, resinous odour, and had the following properties:  $d_{15}^{20}$  0.925;  $\gamma_{15}^{20}$  1.4760; f.p. below -15°C.; saponification value 188.5; iodine value (Wj)s 130.3.

Commercial inukaya oil resembles Kaya oil with which it has been occasionally confused in the literature, but has inferior drying properties; it is used for similar purposes, viz. as a burning oil and for the manufacture of oiled paper, varnishes, etc., but cannot be employed as an edible oil, on account of the resinous odour which is present in even the cold-drawn product.

E. L. and L. I.

**INULASE** (v. Vol. IV, 314b).

**INULIN** (v. Vol. II, 303a).

**INULO-COAGULASE** (v. Vol. III, 31a).

**INVAR**, a 36% nickel steel.

**INVERTASE** (Sucrase, Saccharase) is an enzyme which hydrolyses sucrose (cane-sugar) to *D*-glucose (1 mol.) and *D*-fructose (1 mol.). It occurs in the small intestine of mammals, in the tissues of certain animals and plants and in numerous moulds and fungi. One of the best sources is yeast, invertase being present in all species except *Saccharomyces octosporus*, *S. capsularis* and *S. membranaefaciens* Hans. Active preparations may readily be obtained by allowing the yeast to hydrolyse at 37° in the presence of a little toluene, when liquefaction occurs. Alcohol is added to the aqueous extract and the precipitate extracted with water (O'Sullivan and Tompson, J.C.S. 1890, 57, 834; Euler *et al.*, Z. physiol. Chem. 1910, 69, 152; 1911, 73, 335). Willstätter and Racke (*Annalen*, 1921, 425, 53) carried out the autohydrolysis in a neutral, instead of acidic, medium. Various methods of purification have been used Hudson (J. Amer. Chem. Soc. 1908, 30, 1564) removed

inble proteins and gums by the addition of lead acetate; excess of lead was removed by potassium oxalate and the latter by dialysis. Finally the enzyme was precipitated by alcohol and dissolved in water. More recently, adsorption on kaolin or aluminum hydroxide has been used for purification (Lutz and Nelson, J. Biol. Chem. 1934, 107, 169; Kōsaki, A. 1938, 111, 695). Weidenhagen (A. 1936, 1555) used strontium hydroxide, Richtmeyer and Hudson zinc sulphide and Adams and Hudson bentonite as adsorbents. In the last two cases the extract was adjusted to  $pH$  4.5, and the elution carried out at  $pH$  6.1 (J. Amer. Chem. Soc. 1938, 60, 983). Willstätter has investigated the adsorption of invertase by aluminum hydroxide and by kaolin, finding it most efficient in dilute solution or in the presence of 10% acetic acid (Z. physiol. Chem. 1922, 123, 181; with Schneider, 1924, 133, 193). Invertase may be kept for several years without losing activity.

The activity of these preparations may be measured by observing the rate at which sucrose is hydrolysed under standard conditions. In their classical researches, O'Sullivan and Tompson determined the time in minutes required by

50 mg. of the enzyme to reduce to zero the rotation of 25 c.c. of solution containing 16% of sucrose at the optimum  $p_H$  at 15.5°. Willstätter and Racke (*l.c.*; Willstätter and Kuhn, *Ber.* 1923, **56** [B], 509) adopted a similar procedure. On this basis, brewer's yeast requires 150–400 minutes. Purified specimens can now be prepared with a time value of 0.1–0.2 minutes. Sumner and Howell (*J. Biol. Chem.* 1935, **108**, 51) use the dinitrosalicylic acid method for the estimation of reducing sugars formed. Sufficient invertase is used to obtain about 10 mg. of invert sugar by the hydrolysis of 6 c.c. of 5.4% sucrose in 5 minutes, at 20° and  $p_H$  4.5. Under these conditions the velocity of hydrolysis is great, and the assay is therefore rapid. The reaction is stopped by the addition of 5 c.c. N.-NaOH, and the invert sugar determined colorimetrically with dinitrosalicylic acid.

There has been considerable divergence of views as to the chemical character of invertase, but it appears that both protein and carbohydrate reactions can be obtained (*cf.* Euler and Josephson, *Ber.* 1925, **57** [B], 859; Willstätter and Schneider, *Z. physiol. Chem.* 1924, **133**, 193). The former authors detected tryptophan in their preparations, and this was confirmed by ultra-violet absorption spectrum measurements (Albers and Meyer, *l.c.*, 1924, **228**, 122; *see also* Lutz and Nelson, *l.c.*; Tauber, "Enzyme Chemistry," J. Wiley & Sons, 1937, p. 127). Ultra-filtration experiments upon invertase isolated from the intestinal juices of dogs indicate that it is just retained by a membrane of porosity 10 m $\mu$ . (Grabar, *Compt. rend. Soc. Biol.* 1935, **118**, 455).

The activity of invertase is maximum at 55–60° (*cf.* 35–40° for maltase), but it is destroyed at 65–70° (*see* Chaudun, *Bull. Soc. Chim. biol.*

1936, **18**, 1467). Below 0°, the velocity of inversion decreases only slowly (Kertesz, *Z. physiol. Chem.* 1933, **216**, 229). The kinetics of the process are discussed by Nelson (*Chem. Rev.* 1933, **12**, 1) and by Weidenhagen (*Ergebn. Enzymforsch.* 1932, **1**, 168). T. A. White has examined the kinetics in the light of the theory that sucrose and water are adsorbed by the enzyme before reaction, the adsorbed products inhibiting the hydrolysis (*J. Amer. Chem. Soc.* 1933, **55**, 556). The thermal changes have been measured by Kōsaki (*A.* 1937, **111**, 180; 1938, **111**, 695).

The optimum  $p_H$  for yeast invertase is 4.5 (Michaëlis and Davidsohn, *Biochem. Z.* 1911, **35**, 386), whereas maltase (also present in yeast) is inactive at this  $p_H$ . Even minute amounts of alkali may inhibit the action, and care is necessary to buffer the  $p_H$  during quantitative work. The retarding effect of CN<sup>-</sup> and of pectin is ascribed to the increased  $p_H$  (Manchester, *J. Biol. Chem.* 1939, **130**, 439). The action of basic and acidic dyes is discussed by Quastel and Yates (*Erzymologia*, 1936, **1**, 60).

Invertase will hydrolyse fructofuranosides other than sucrose. The trisaccharides raffinose and gentianose and the tetrasaccharide stachyose are also attacked by yeast invertase (Kuhn and Munch, *Z. physiol. Chem.* 1925, **150**, 220; 1927, **163**, 1). Weidenhagen has shown that large amounts of the enzyme will hydrolyse the polysaccharides inulin and inulin to fructose (*A.* 1933, 1080). The activity with regard to these substrates varies considerably according to the source of the invertase (*e.g.* from *Aspergillus oryzae*, *Penicillium glaucum*).

The chemistry of invertase has been reviewed by J. M. Nelson (*Chem. Rev.* 1933, **12**, 1).

G. T. Y.



# INDEX TO VOLUMES I—VI

THE Index contains about 17,550 entries arranged alphabetically, and familiar inversions and abbreviations have been employed. For reasons of economy many inverted entries have been printed without a final "of," and the word "dyes" has been indexed instead of "dyestuffs." The letters *a, b, c, d* attached to references indicate consecutive quarters of a page. Titles of articles are located by clarendon numerals.

The space available did not allow of indexing all the synonyms, italicised words and technical terms to be found in the text, but it is hoped that the choice made will be acceptable.

The Index is not intended to solve all relevant questions of spelling, hyphening and nomenclature, but when the text has not been followed it is believed that the reason for the alteration will be evident.

Preliminary work on the indexing of Vols. II and III was done by Dr. A. H. Cook, to whom acknowledgment is made. Acknowledgments for skilled assistance are made to Miss E. Wilkinson, Miss V. Goring Thomas, Miss B. Whiteing, and Mr. G. Bird.

J. N. GOLDSMITH.

## A

- A-Acid**, I. 1a  
 **$\alpha$ -Acid**, I. 1a  
**Abaca fibre**, I. 1a; V. 104d  
**Abaku nuts**, I. 655a  
**Abalak**, I. 1a  
**Abalone**, I. 1a  
**"Abalyn"**, I. 1b  
**Abasin**, I. 1b  
**Abassi cotton**, I. 1b  
**Abderhalden reaction**, I. 1b  
**"Abdocain"**, I. 1b, 369a; II. 34b  
**Abel heat test**, III. 363d; IV. 243d, 547a  
 — — —, Gutmann's modification, IV. 547c  
**"Abelite"**, I. 1b  
***Abelmoschus moschatus***, I. 304a; IV. 591a  
***Abies* spp.**, I. 1c, 450b; II. 237c  
**Abietenes**, I. 1c, d  
**Abietene**, sulphonated, as wetting agent, I. 1d  
**Abietenol**, I. 2a  
**Abietic acid and derivatives**, J. 2a; II. 261b; III. 205c  
 — — —, detection and detn., I. 3b  
 — — —, methyl esters, I. 1a  
 — — —, salts, I. 2c  
**"Abisol"**, I. 3c  
**"Abracol"**, I. 3d  
**Abralin**, I. 4d  
**Abranin**, I. 4d  
**"Abrasil"**, I. 3d  
**Abrasives**, I. 3d  
 —, boron carbide and boron silicide, I. 4a; II. 44c, 50d  
**"Abrastol"**, I. 4c; IV. 30a  
**Abraum-salts**, II. 390a  
**Abrin**, I. 4d  
**Abrine**, I. 4d  
**"Abrodil"**, I. 4c  
***Abroma augusta***, I. 4c  
**Abrotine**, I. 4c  
***Abrus precatorius***, I. 4c  
**Absinth**, I. 4d  
 —, essential oil, I. 5c  
**Absinthin** or absinthiin, I. 5d
- Absinthol**, I. 6a  
**"Absorbite"**, I. 6b  
**Absorptiometer**, spectroscopic, III. 305d  
**Absorption** (see also Washers), I. 6b  
 —, counter-current, in towers, I. 7d  
 — spectra in analysis, II. 709a  
**Abutic acid**, I. 11a  
***Abutilon indicum***, *A. avicennae*, I. 11b; V. 161c  
**Abyssinian Gold**, I. 11b  
**Acacatechin**, I. 11b; II. 434a  
**isoAcacatechin**, II. 435c  
**Acacatin**, I. 11b  
***Acacia arabica***, *A. spp.*, I. 11c, 585b  
**Acacia bark**, I. 11c  
 — catechu, I. 11c  
***Acacia cavena***, I. 11c  
 — dealbata (see also *Acacia* bark), I. 11c  
 — *Jarvesiana*, I. 11c; IV. 394c  
 — *senegal*, I. 11d; VI. 155d  
**Acaciin**, I. 12b  
**Acacipetalin**, VI. 85b  
**Acajou**, cashew nut, I. 12b, 365d  
***Acalypha indica***, I. 12b  
**Acalyphine**, I. 12b  
**Acanthite**, I. 458c  
**"Acardite"**, IV. 14d  
**Acaroid resins**, I. 12b  
**Accelerators**, I. 12b  
**Acceptor**, I. 12c  
**"Acedicoin"**, I. 12c  
**"Acedicone"**, I. 12c  
**"Acedronoles"**, I. 12c  
**Acenaphthene**, I. 12c  
**Acenaphthanol**, I. 13a  
**"Acerdol"**, I. 14a  
**Aceridin**, I. 14a  
**Aceritol**, I. 14a  
***Acer saccharinum*** or *A. saccharum*, I. 14a  
**Acertannin**, I. 14a; VI. 85b  
**Acetal**, amino-, I. 35d  
 —, chlorotriethylphosphino-, I. 36a
- Acetaldehyde**, I. 14a, 20d  
 — and ammes, condensation products from, I. 29b  
 —, chain photolysis, I. 30a  
 —, chloro-, from acetylene, I. 91b  
 —, cyanohydrin, I. 21b  
 —, dichloro-, I. 21c  
 —, disulphonic acid, I. 84a  
**"Acetaldehyde - ethyl acetate"**, I. 35b  
**Acetaldehyde** from acetylene, I. 16a  
 — — —, by-products in production of, I. 19b  
 — — —, alcohol, I. 15a; II. 427d  
 — — — *Aspergillus niger*, V. 51b  
 — — — yeast, II. 90b  
 — — — in caffee, II. 198b  
 — — — production of aldol, butyl alcohol, crotonaldehyde and ethyl acetate, I. 26b, 28a  
 —, luminescent polymerisation, III. 23b  
 —, monochloro-, I. 21c  
 —, oxidation products, I. 23c, 24a, 25b  
 —, prepn., II. 427d  
 —, reduction to alcohol, II. 426d  
 — synthetic resins, I. 29a  
 —, — rubber from, I. 30b  
 —, tribromo-, II. 106a  
 —, trichloro-, I. 21c; III. 34d  
 —, unclassified reactions, I. 29d  
**Acetal**, mono- and di-chloro-, and bromo-, I. 35c, d  
 —, moniodo-, I. 35d  
 —, nitro-, I. 35d  
**Acetals**, I. 32a; IV. 382d  
 —, aromatic, I. 37a  
 —, cyclic, I. 33c  
 —, hydrolysis, VI. 252a  
 —, methenal, of aromatic glycols, I. 37a  
 —, mixed, I. 33c  
**Acetal sulphide**, I. 30a  
 —, trichloro-, I. 35c

- Acetamide**, I. 59d  
**Acetanilide**, I. 38d  
 —, *p*-bromo-, I. 30a  
 —, *N*-chloro-, I. 30a  
 —, *p*-chloro-, I. 30a  
 —, *o*- and *p*-nitro-, I. 30a  
**Acetannin**, I. 39b  
 "Acetarsol," I. 39c, 489c  
 "Acetarsone," I. 39c, 489c  
**Acetate**, iron, mordant, II. 53d  
 — rayon, *see* Cellulose acetate;  
 Fibres artificial or rayon.  
**Acetates**, acetic acid, qualitative  
 reactions, I. 53b; II. 569d; V. 297a  
**Acetate** silk dyes, I. 39c, 205c;  
 IV. 127b, 234b  
**Acetegenol**, I. 43b; IV. 306d  
**Acet-isoegenol**, I. 43c; IV. 300d  
**Acetic acid**, I. 43c  
 —, acetamino-, VI. 73a  
 —, amino-, VI. 71d  
 — as preservative, IV. 28a  
 —, chlorobromo-, VI. 176a  
 —, chloro-, from acetylene,  
 I. 91b  
 —, density of aqueous solu-  
 tions, I. 52  
 —, detn., I. 53b  
 —, diazo-, ethyl ester, III. 599a  
 —, dibromo-, VI. 175d  
 —, dichloro-, VI. 175a  
 —, dichloromonobromo-, VI. 176b  
 —, di-iodo-, VI. 176c  
 —, esters, I. 50b  
 —, fluorodibromo-, ethyl  
 ester, VI. 176d  
 —, formation from methyl  
 alcohol, II. 350c  
 —, from acetylene, I. 50b,  
 80d  
 —, carbon monoxide, I. 51a  
 —, ethylidene diacetate, I. 51b  
 —, formaldehyde, I. 51a  
 —, methane, I. 50d  
 —, methyl alcohol, I. 50d  
 —, formate, I. 51a  
 —, hydroxy-, V. 73c  
 —, in caffeeol, II. 198b  
 —, monobromo-, VI. 175d  
 —, monochloro-, VI. 174c  
 —, acid chloride, VI. 175a  
 —, monochlorodibromo-, VI. 176b  
 —, monoiodo-, VI. 176b  
 —, prepn., II. 310d, 425c,  
 427d  
 —, qualitative reactions, *see*  
 Acetates.  
 —, salts, I. 54a  
 —, solidification point of  
 aqueous solutions, I. 51c, d  
 —, triazo-, VI. 298d  
 —, tribromo-, VI. 176a  
 —, trichloro-, I. 65a; VI. 175b  
 —, diethylaminoethyl  
 deriv., VI. 175c  
 —, in toxicology, VI. 175b  
 —, trifluoro-, VI. 176d  
 —, tri-iodo-, VI. 176c  
 — anhydride, I. 57b  
**Acetic anhydride**, analysis, I. 59b  
 —, detection in acetic acid,  
 I. 53d  
 — esters, synthetic production,  
 I. 51a, 84c  
**Acetin** or acetine, I. 60b  
 — as plasticiser, II. 448c  
**Acetoacetanilide**, I. 61b  
**Acetoacetic acid**, I. 61b  
 —, detection in acetic acid,  
 I. 53d  
 — 2:4-dinitrophenylhydra-  
 zone, I. 61b  
 — esters, I. 61d  
**Acetobacter suboxydans**, V. 330d;  
 VI. 495c  
**Acetobetaine**, I. 680a  
 "Acetocaustin," I. 65a  
**Acetochloroamide**, I. 60a  
**Acetocitric acid**, III. 186b  
**Acetoin**, I. 140c  
**Acetol**, I. 65a  
 — acetate, I. 65c  
 "Acetol," I. 65c  
**Acetol**, Baudisch test for, I. 65c  
 —, ethyl ether, I. 65b  
 —, hydroxyacetone, I. 65a  
**Acetomorphine**, VI. 205d  
 — hydrochloride, I. 65c  
**Acetonaphthone**, I. 65d  
**Acetone**, I. 65d  
 —, acetyl-, I. 70a  
 —, bromination, II. 320b  
 —, bromo-, I. 69d  
 —, in chemical warfare, III. 10c, d.  
 —, chloro-, I. 69b  
 — chloroform ("Chlorotone"),  
 I. 70c, 371c; III. 36c  
 —, chloro-, in chemical warfare,  
 III. 10c, 11a  
 —, compounds with sugars, II. 289d  
 —, cyanohydrin, I. 68d  
 —, detn., I. 68a; IV. 532b  
 —, in vapours, II. 681d  
**Acetonedicarboxylic acid**, I. 70a, 70d; III. 185d  
**Acetone** ethylacetal, I. 36d  
 — from acetylene, I. 81b  
 — horse-chestnuts, VI. 279d  
 — glycerol, VI. 60a, 70c  
 —, halogenation, VI. 250b  
 —, halogen-substituted derivs.,  
 I. 69b, c, d  
 —, hydroxy-, I. 65a  
 — in dopes for film manu-  
 facture, II. 448c  
 — urine, detection, I. 67c  
 —, iodo-, prepn., III. 11d  
 — methylacetal, I. 36d  
 — oil, I. 70d  
 — phenylhydrazone, I. 69b  
 — phosphate, dihydroxy-, re-  
 actions in muscle, VI. 76d  
 — production by bacterial fer-  
 mentation, II. 189d, 429b,  
 471d; V. 45a  
 —, pseudocyclocitralidene, I. 70a  
 — recovery, III. 302c; V. 123d  
 —, reduction to isopropyl al-  
 cohol, II. 426d  
 — semicarbazone, I. 69a  
 —, solvent in lacquers, II. 469d  
 —, specifications, II. 472b  
**Acetonitrile** from acetylene, I. 84b  
**Acetonylacetonones**, metallic,  
 co-ordination, III. 329a,  
 335b  
**Acetophenone**, I. 71a  
 —, *m*-, *o*- and *p*-amino-, I. 71c  
 — ammonia, I. 71b  
 —, benzal-, or benzylidene-, I. 71d, 190a  
 —, *p*-bromo-, I. 71d  
 —, chloro-, in chemical warfare,  
 III. 9a  
 —, —, prepn., III. 11a  
 —, diethylacetal, I. 71b  
 — in castor, II. 419d  
 —, *m*-nitro-, I. 71c  
 — phenylhydrazone, I. 71b  
 — oxime, I. 71b  
**Acetophenones**, hydroxy-, VI. 399d  
**Acetophenone**, 2:4:6-trinitro-,  
 I. 71c  
 **$\beta$ -Acetopropionic acid**, I. 71d  
**Acetopurpurine B B**, I. 73b  
 "Acetopyrine," I. 73b  
 "Acetosol," I. 517d  
 "Acetoxane," I. 73b  
**Acetoxime**, I. 69a  
 "Acetozone," I. 73b; IV. 28a  
**Acetylacetone**, rare earth  
 derivs., II. 515d  
 "Acetylaladin," I. 11a  
**Acetyl-benzoyl peroxide**, IV. 28a  
**Acetylcarbinol**, I. 65a  
**Acetylcellulose** (*see also* Fibres  
 artificial or rayon), II. 464d  
**Acetyl chloride**, trichloro-, I. 105c  
**Acetylene**, I. 73b  
 — as illuminant, I. 116c  
 —, bromo-derivs., I. 82d, 83a, b  
 —, calcium carbide for manu-  
 facture of, II. 219b  
 —, carbon tetrachloride from,  
 II. 354d  
 —, carcinogenic compounds  
 from, II. 378c  
 —, chlorine derivs., I. 96c  
 —, detection, I. 96a; II. 681c  
 —, detn., gasometric, I. 96a; II. 677d, 681c  
 —, dichloride, IV. 7b  
 —, dichloro-, I. 90d  
 —, divinyl, I. 88b  
 — from calcium carbide, I. 107b  
 — ethane, I. 76d  
 — ethylene, I. 76a  
 — methane, I. 76a  
 — generators, I. 109c  
 —, heavy, I. 79c  
 —, industrial uses, I. 106c  
 —, iodo-derivs., I. 83c  
 —, metallic derivs. (*see also* Car-  
 bides; individual metals),  
 I. 82a  
 —, methyl, *see* Allylene.  
 — phenol condensation pro-  
 ducts, I. 85a  
 —, polymerisation reactions, I. 85b  
**Acetylenes**, mono- and di-  
 substituted, I. 117c  
 —, sodio-compounds, reaction  
 with carbon dioxide, II. 363c  
 —, —, —, ethyl carbon-  
 ate, II. 363d  
**Acetylene**, structure, I. 79c  
 — tetrabromide, IV. 357d

- Acetylene** welding, I. 112d  
**Acetyl-H-acid**, I. 119d; IV. 207c  
**Acetylidene**, dibromo-, II. 320c  
**Acetylidene tetrabromide**, IV. 357d  
**Acetylmethylcarbinol** in bread, II. 80c  
**Acetyl peroxide**, antiseptic, IV. 28a  
 —, prepn. II. 373a  
 — radical, detn., II. 625c  
**Acetylsalicylic acid**, I. 119d, 517d  
 —, calcium salt, I. 370a, 517d  
**Acheson** graphite, I. 119d  
 "Achromin," I. 119d  
**Achillea millefolium**, I. 119d  
 "Achiodin," I. 120a  
**Achras sapota**, I. 120a  
**Achroodextrin** II and III, III. 569a, b  
**Acid** Alizarine azo dyes, I. 120a  
 — dyes, I. 404a  
 — anhydrides, I. 57a; II. 370c, d, 376c  
 — base catalysis, VI. 255b  
 — pairs, conjugate or corresponding, VI. 248b  
 — Chrome dyes, I. 120a  
 — constants, VI. 248d  
 — definition, VI. 247a, 249a  
 — dyes, IV. 126d  
 — Fuchsin, I. 120a  
**Acidimetry** and alkalimetry, II. 637c  
**Acid-mordant dyes**, IV. 127d, 128b  
 — number of porphyrins, III. 82a  
 — of Bayer's patents, I. 658c  
**o-Acid** of Claus and Volz, I. 658  
**Acid** of Schultze, I. 658c  
 "Acidol," I. 120b, 686b  
**Acidolysis**, IV. 349d; VI. 397a  
**Acids** and bases, theory, VI. 247a  
 —, mineral, solvent action, II. 549b  
 —, organic, detn., potentiometric, II. 708a  
 —, with ceric sulphate, II. 510c  
 —, strength, VI. 248c  
 "Acidulin," I. 120c  
**Acid** wool dyes, I. 205c  
 "Acitrin," I. 120d  
**Acker** electrolytic cell, III. 57b  
**Acocanthera schimperii**, I. 120d  
 "Acoine," I. 120d, 360c; VI. 144a  
**Aconic acid**, I. 120d  
**Aconine**, I. 121d  
**pseudoAconine**, I. 123a  
**Aconitic acid**, I. 120d  
**Aconitine** and aconite alkaloids, I. 120d  
**pseudoAconitine**, I. 123b  
**Aconitum napellus**, I. 120d  
 —, A. spp., I. 120d, 122c, 123a, 638c  
 "Acopyrin," I. 73b  
**Acorn**, I. 124b  
**Acorn** oil, I. 124a  
**Acorus calamus**, and essential oil, I. 124b; II. 201a  
**Acraldehyde**, I. 136a  
**Acridan-nitrile**, I. 127b  
**Acridine**, I. 124c, 565a  
 — and acridinium, diamino derivs., I. 134d  
 — 5-carboxylamide, I. 127b  
 — 5-carboxylic acid, I. 127b  
 — 5-chloro-, I. 129b  
 — 5-cyano-, I. 127b  
 — 2,6-diamino-, I. 135a  
 — 2,8-diamino-5-o-carboxy-phenyl-, I. 125d  
 — 2,8-diamino-, compound of arsonic acid, I. 134d  
 — drugs, I. 133d  
 — 3-ethoxy-5:8-diamino-, I. 131a  
 — Grignard compounds, I. 127b  
 — hydrochloride, 2-amino-3-methyl-8-dimethyl-, I. 132b  
 — 5-hydroxy-N-oxide, I. 129a  
 — N-oxide, I. 129a  
 — 5:10-peroxide, I. 129a  
 — salts, I. 127b  
**Acridinium**, quaternary salts, I. 126c  
**5-Acridol**, I. 128d  
**Acridone**, I. 128c, 135d  
 — 3-arsonic acid, I. 129b  
 — 1-bromo-4-nitro-, I. 129b  
 — 5-chloro-2:6-dinitro-, I. 135a  
 — 1-chloro-4-nitro-, I. 129b  
 — colours, I. 417b  
 — 2:8-diamino-, I. 125b  
 — 2:8-dihydroxy-, I. 129b  
 — dimethoxy-, I. 129b  
**Acridones** derived from anthraquinone, I. 396a  
**Acridone-3-stibonic acid**, I. 129b  
 — 2-sulphonic acid, I. 125b  
**Acriflavine** (see also Flavine), I. 134a, b, 135d; IV. 30b  
**Acrylyl thiocyanate** and isothiocyanate, I. 136a  
**Acrolein**, I. 136a; III. 10d  
**Acrolein** ethylacetal, I. 36a  
**Acrolein** resins, I. 136d  
 "Acrolite," I. 136d  
**Acrose**,  $\alpha$ -, and  $\beta$ -, I. 136d  
**Acrylic acid**, I. 137a  
**Actaea racemosa**, I. 137a  
 "Acterol," I. 137b  
**Actinine**, II. 392a  
**Actinioerythrin**, I. 137b; II. 401c  
**Actinium**, I. 137b  
**Actinolite**, I. 499c  
**Actinon**, I. 138c  
**Actinozoa** spp., coral from, III. 360c  
**Activators**, V. 203d  
 "Activin" (see also "Aktivin"), I. 140a  
**Activity**, chemical (see also Catalysis, homogeneous), II. 537b  
 "Actol," I. 140b  
 "Acton," I. 140b  
**Actor**, I. 12c  
**Acyl azides**, I. 582b  
 — cyanides, prepn., II. 376b  
 — halides, prepn., II. 376b, 376b  
**Acylolins**, I. 140b  
**Acyl peroxides**, prepn., II. 373a  
 "Adalin," I. 141a  
**Adamite**, I. 4a; 141a  
 "Adamon," I. 141a  
**Adansonia digitata**, I. 141b  
**Adenase**, IV. 315a  
**Adenine**, I. 141b; II. 197a; VI. 153a  
**9-Adenine-methyl-thio-pentoside**, VI. 85c  
 "Adenas," I. 142a  
**Adenosine**, I. 142a; VI. 85c  
 — desamidase, IV. 315a  
**Adenylic acid**, I. 142a; II. 287b; IV. 311b  
**Adenylpyrophosphate**, V. 18b  
 — creatine reaction, VI. 78b  
 — in lactic acid formation, V. 34d; VI. 77a, 78a  
 — muscle extract, VI. 75c  
**Adeps colli equini**, VI. 280c  
**Adhesives**, I. 142b  
 —, casein in, II. 414b  
**Adipic acid**, I. 143c  
**Adipic anhydride**, I. 144a  
**Adipocellulose**, II. 407a  
**Adipocere**, I. 144c; II. 25d  
**Adipodialdehyde**, I. 144a  
**Adipyl dichloride**, I. 144a  
**Adlumidine**, I. 145b  
**Adlumine**, I. 145a  
**Admiralty gun-metal**, I. 145b  
 — white-metal, I. 145b  
 "Adnephryn," I. 147d  
 "Adnuc," I. 145b  
**Adonidoside** (see also Adonis vernalis), II. 387b; VI. 85c  
**Adonis vernalis**, I. 145b; VI. 85c  
**Adonitol**, I. 145c; II. 290b  
**Adonivernoside**, II. 387b; VI. 85c  
**Adrenaline**, I. 145c  
 — in food poisons, II. 388a  
 — substitutes, I. 147c  
 "Adrenamine," I. 147d  
**Adrenosterone**, VI. 278b  
 "Adronol," I. 147d  
**Adsorbents**, commercial, I. 155a; II. 315c; III. 270d; IV. 246d  
 "Adsorbit," I. 147d  
**Adsorption**, I. 147d; III. 282b  
 —, activated, II. 540a; VI. 214b, 314d, 373b, 377c, 380b  
 — in catalysis (see also Catalysis, heterogeneous), II. 422d  
 —, "molecular," VI. 315a  
 "Adurol," I. 155b  
**Adynerin**, II. 380c  
**Egrine**, I. 450b  
**Egle marmelos**, I. 155c, 585d  
 "Aeral," I. 253a  
**Aerated** and mineral waters, I. 155c  
 "Aerofloat 15, 25 and 31," V. 205d  
 "Aeron," I. 160a, 277a  
**Aerosols**, I. 160a  
 "Aerosols," V. 207d  
**Erugo**, I. 160b; III. 33b  
**Eschynite**, I. 160b; II. 512b  
**Escigemin**, I. 160c  
**Escin**, I. 160c; VI. 85c  
**Esculetin**, I. 160c  
 —, methoxy-, III. 117d  
**Esculinic acid**, III. 27b  
**Esculic acid**, III. 27b  
**Esculin**, I. 160c; III. 27a, 413a; VI. 279c  
**Esculus hippocastanum**, I. 238d; VI. 279b  
**Esculus** spp., I. 238d; VI. 88b, 279b

- "*Æthacol*," I. 160d  
 "*Æthocaine*," or Ethocaine, I. 1b, 160d, 309a; II. 31b  
 "*Æthone*," I. 160d  
*Æthusa cynapium*, I. 160d; III. 324d  
*Ætiocholanolic acid*, from digitoxigenin, II. 382b  
*Ætioallocholanolic acid*, from uzarigenin, II. 382b  
*Ætiocholanone*, relation to cholesterol, III. 90b  
*Ætioporphyrin*, III. 83a; VI. 102a  
 —, relation to blood pigments, II. 20c  
 "*Ætox*," V. 305d  
*Aframomum amaniense*, I. 160d  
 — *malu*, I. 161a  
 — *melegueta*, I. 161a  
*African marigold*, I. 161a  
 "*Afridol*," I. 162b  
*Afterdamp*, II. 323d, 344c  
*Atwillite*, I. 162b; II. 150c  
*Agalite*, I. 162b  
*Agalmatolite*, I. 162c  
*Agar-agar*, I. 162d, 199b  
 — — — gel, III. 290d  
 — — — reactions, I. 163b  
*Agarobilla*, see *Algarobilla*.  
*Agate*, I. 163c; II. 517c  
*Agate-amygdaloides*, I. 163d  
*Agathic acid*, I. 164d  
 "*Agathin*," I. 165a  
*Agave*, I. 165a  
*Agave spp.* and fibres, I. 165a; V. 160a, 168b  
*Agavose*, I. 165a  
*Ageing*, I. 165b  
*Agfacolor film*, II. 440d  
*Agfa Ultra Colour film*, II. 453a  
*Aglycone*, VI. 82c  
*Agmatine*, I. 171c; VI. 144a  
*Agmatine* in ergot, IV. 331d  
*Agmolin*. See *Lanolin*.  
*Agnoosterol*, III. 92d  
*Agon*, IV. 347d  
 "*Agonol*," I. 171d  
*Agropyron repens*, I. 171d  
*Agrostis pasture*, VI. 132c  
 "*Agurin*," I. 171d  
 "*Aguttan*," I. 171d  
*Ahouain*, II. 386c  
 "*Aich metal*," I. 171d  
*Ailanthus silk*, *A. glandulosa*, I. 171d  
*Air-conditioning plants*, VI. 287a  
 — drying plant, IV. 78a  
 — — — silica gel, IV. 79a  
 — liquid, fractionation, II. 424b  
 "*Airoform*," I. 171d  
 "*Airogen*," I. 171d  
 "*Airol*," I. 171d, 700d  
*A.I. Rounkol explosive*, IV. 550b  
*Ajacine*, I. 172a; III. 550d  
*Ajaconin*, III. 550d  
*Ajowan oil*, I. 172a  
 "*Akardit*," I. 172a  
*Akariton fat*, IV. 80d  
*Akrochordite*, I. 172a  
 "*Aktivin*" (see also "*Activin*"), I. 172b  
 "*Aktoprotein*," I. 172b  
 "*Akund*," V. 189b  
*Alabandite*, I. 172b  
*Alabaster*, I. 172b; II. 232b; VI. 159c  
*Alacreatine*, I. 410b  
*Alaite*, I. 172d  
*Alarnosite*, I. 172d  
*Alanine*, I. 172d  
 —, acyl derivs., I. 174b  
 $\beta$ -Alanine, I. 175a; II. 392c  
 $\alpha$ -Alanine anhydride, I. 174a  
*Alanine salts*, I. 173d  
*Alanol*, IV. 328c  
*Alantolactone*, alantolic acid, I. 175b  
*Alant root*, I. 175b  
*cycloAlanylalanine*, I. 174a  
*Alban* or *Albane*, I. 175c; VI. 158d  
 — "*Albany slip*," VI. 9d  
 "*Albargin*," I. 175c  
*Alba-saponin*, VI. 89b  
*Albaspidin*, I. 175c; V. 181c  
*Albertite*, I. 175c  
 "*Albertols*," I. 175d  
*Albite*, I. 175d, 204d; V. 1d  
 "*Albocarbon*," I. 175d  
*Alboleersin*, V. 50d  
*Album græcum*, I. 175d  
*Albumin*, blood serum, II. 19c  
*Albuminoid ratio*, IV. 601b  
*Albuminoids* in plant analysis, IV. 593d  
*Albumin*, oxidation, II. 278b  
 — phenol from, II. 303d  
*Albumins*, rice, II. 493b  
 "*Alclad*," I. 253a, 275b  
*Alcohol* (see also *Ethyl alcohol*), I. 175d  
 —, absolute, prepn., I. 103c, 176b, 178b  
 —, —, tests, I. 180d  
*Alcoholase*, I. 20b  
*Alcohol denaturants*, I. 183c  
 —, defn., II. 683a  
 —, mochl., I. 692d  
*Alcoholometer*, 'Tralles', I. 188c  
*Alcoholometry*, I. 185b  
*Alcohols*, fatty, from fats, II. 427b  
 —, —, prepn. by catalytic hydrogenation, VI. 183c  
 — for motor fuels, I. 192a  
 — from carbon monoxide (see also *Fischer-Tropsch synthesis*), II. 350b, c, 425c  
 — petroleum, I. 192c  
 —, oxidation to acids, II. 362a  
*Alcohol standards*, I. 179c  
*Alcoholysis*, IV. 349d; VI. 397a  
*Alcornin* or *alcornol*, I. 193c  
*Aldehyde-ammonia*, I. 22a  
 — — — resins, I. 21a, 29a  
*Aldehydes*, I. 193c  
 —, action in bread, II. 82a  
 —, compounds with sugars, II. 289d  
 — from carbon monoxide, II. 350b  
 —, luminescent oxidation, III. 23c  
 —, oxidation, II. 362a  
 —, prepn., II. 373c  
*Aldehydines*, I. 197d, 310a  
*Aldehydrol*, I. 21a  
*Alder bark*, I. 197d  
 — *Buckthorn bark*, I. 198a  
*Aldol*, I. 20b, 198a  
*Aldolase*, V. 25d, 26c  
*Aldol condensation*, I. 20b, 195d, 198a; II. 123b  
 — —, boron fluoride catalyst, VI. 259d  
*Aldoses*, detection, II. 293c  
 "*Aldrey*," I. 253a, 277a  
 "*Aldur*," I. 198b  
 "*Aldural*," I. 253a  
*Ale*, II. 104d  
*Alén's* ( $\alpha$ -) acid, V. 329d  
 "*Aletodin*," I. 517d  
 "*Aleudrin*," I. 198b  
*Aleurites spp.*, I. 198b; IV. 82a, 83c  
*Aleurone grains*, I. 198c  
*Alexandrite*, III. 119a  
 "*Alexandrite*, synthetic," V. 512d  
 "*Alexipon*," I. 199a  
*Alfa*, I. 199a  
*Alfalfa*, I. 199a  
 — meal, IV. 506b  
*Alformant lamp*, IV. 27b  
*Algæ*, I. 199a  
 —, products from (see also *Iodine*), I. 162d, 199a; II. 403c; III. 390c  
*Algaroba*, I. 201b  
*Algarobilla*, I. 201b; IV. 276d  
*Algaroth*, Powder of, I. 201b, 448a  
*Algarrobin*, I. 201b  
*Algin*, I. 199d, 200a, 201d  
*Alginase*, I. 201d  
*Alginic acid*, I. 200a, 201d; II. 298a  
 — —, salts, I. 202a  
*Alginoid iron*, I. 203a  
 "*Algiron*," I. 203a  
*Algodonite*, I. 203a; IV. 55b  
*Algol colours*, I. 232c, 410a, 418d, 420a  
 — vat dyes (see also *Vat dyes*), I. 200a  
*Alipite*, V. 430a  
*Alite*, II. 141b  
 "*Alival*," I. 203b  
*Alizarin* (see also *Anthracene*; *Anthraquinone*; *Chay root*; *Madder*), I. 203b  
 — and allied dyes (see also *Anthraquinone*; *Anthraquinone dyes*; *Dyeing*; *Vat dyes*), I. 203b, 212d, 402d  
 — —, 4-amino-, I. 206b, 228b  
 — *Astrol*, I. 200a  
 — B, I. 405d  
 — BG, I. 231c  
 — Bordeaux, see *Quinalizarin*.  
 — Brilliant Cyanine GG, I. 228d  
 — 3-bromo-, I. 220c  
 — Cardinal, I. 228b, 393b  
 — Celestol, I. 230d  
 — 3-chloro-, I. 220c  
 — colours, Acid, I. 120a, 404a  
 — Cyanine, I. 205b  
 — G, K, I. 228c, 227b  
 — WRS, I. 230b, 391d  
 — Cyclamen R, I. 232b  
 — Delphinol, I. 230c  
 — diethyl ether, I. 220c  
 — dimethyl ether, I. 220c  
 — -3:5- and -3:8-disulphonic acids, I. 230a  
 — -3:8- and -3:7-disulphonic acids, I. 390b  
 — dyeing, Turkey-red oils in, II. 421d  
 — dyes, diagram, I. 206  
 — Emeraldol G, I. 230d, 393b  
 — from madder, V. 416c  
 — Garnet, I. 206a, 228b  
 — GD, I. 225a



**Alizarin** Geranol B, I. 232*b*, 233*b*, 407*a*  
 — G, GD, I. 224*d*, 225*a*  
 — Gl, I. 224*d*  
 — glycosides, I. 233*b*  
 — Hexacyanin, I. 213*a*, 227*c*, 392*a*  
 — in chay root, II. 523*d*  
 —, 3-iodo-, I. 220*c*  
 — Irisol, I. 206*a*, 231*a*  
 — R, I. 405*b*  
 — manufacture, I. 216*d*, 402*c*  
 —, Perkin's process, I. 218*a*  
 —  $\alpha$ -methyl ether in chay root, II. 523*d*  
 —  $\beta$ -methyl ether, I. 220*b*  
 — 3-monosulphonic acid, I. 390*b*  
 —,  $\alpha$ - or 4-nitro-, I. 228*a*  
 —,  $\beta$ - or 3-nitro-, I. 200*b*, 228*a*  
 — Pentacyanin, I. 227*b*  
 — Powder W, I. 229*d*  
 — production, I. 216*d*  
 —, properties and detection, I. 210*a*, *b*  
 — quinoline, I. 206*b*  
 — RG, SD†, VG, I. 224*d*  
 — Rubinol, I. 206*a*  
 — G, R, I. 232*a*, 400*d*  
 — Saphirol, I. 205*b*, 393*d*, 394*c*  
 — A, I. 230*d*  
 — B, SE, I. 200*a*, 403*b*, 405*a*  
 — SDG, VG, I. 224*d*  
 — 3-sulphonic acid, I. 200*b*  
 — Uranol B, I. 407*b*  
 — R, I. 231*c*, 407*b*  
 — VG, I. 224*d*  
 — Viridine, I. 232*a*  
 —, FF (By), I. 404*c*  
**Alkalbir**, III. 549*a*  
**Alkali-beryl**, I. 684*c*  
 — cellulose, viscose process, V. 117*d*  
 — "Alkali, dense" or "light," for glassmaking, V. 500*d*  
**Alkali metals**, detn., electrolytic, II. 699*d*  
 —, rare, qualitative reactions, II. 550*c*, 563*b*  
**Alkalis**, detn. in clays, III. 203*c*  
 —, —, rocks, II. 585*c*  
**Alkaloid borates**, II. 50*c*  
**Alkaloids** (in general), I. 233*c*  
 —, classification, I. 236*c*  
 —, detn., I. 230*a*  
 —, tests for, I. 235*a*  
**Alkaloid V**, VI. 200*d*  
**Alkanet**, I. 236*d*  
**Alkanna**, Alkannin or Alkenna, see Alkanet.  
**Alkarsin**, II. 188*c*  
 — "Alkasal," "Alkasol," I. 238*c*  
 — "Alkasil," I. 238*c*  
 — "Alkyd" resins, I. 238*c*; II. 469*a*; VI. 64*a*  
**Alkylacetylenes**, I. 117*d*  
**Alkylacridines**, I. 127*c*  
**Alkyladipic acids**, I. 144*b*  
**Alkylbenzenes**, bromination, II. 320*c*  
 **$\beta$ -Alkyl- $\Delta^{\alpha\gamma}$ -butadienes**, I. 89*d*  
**Alkynaphthalenes**, I. 406*d*  
**Allantie** (see also Orthite), I. 238*c*; II. 512*b*  
**Allantoin**, *d*-, *dl*- and *l*-, I. 238*c*  
**Allantoinases**, I. 239*d*, 240*a*  
**Allantoin**, detn. in urine, I. 240*a*

**Allantoin**, prepn., from uric acid, I. 239*b*  
**Allermontite**, I. 439*d*  
**Alenes**, I. 240*b*; II. 156*b*  
**Allen-Moore** electrolytic cell, III. 53*c*  
**Alligator pear**, I. 560*b*  
 — "Allonal," see "Allonal."  
**Aluminium**, V. 429*a*  
**Allium sativum**, A., spp., V. 429*a*  
 — *schoenoprasum*, III. 34*c*  
**Allobarbitone**, III. 573*a*  
**Allocholesterol**, III. 91*c*  
 — "Allochrysine," I. 241*d*; VI. 119*b*  
**Allocryptopine**, I. 241*d*; II. 528*a*  
**Alloelaphite**, I. 241*d*  
**Alloelactose**, I. 242*a*  
**Allomerisation** of chlorophyll, III. 84*d*  
 — "Allonal," I. 242*a*, 623*a*  
**Allophane**, III. 106*a*  
**Allophanic acid**, santalyl ester, I. 212*a*  
 — "Allosan," I. 242*a*  
**Allose**, I. 242*a*; II. 286*a*  
**Allotropy**, I. 242*a*  
**Alloxan**, I. 243*d*  
 —, alkyl derivs., I. 245*b*  
 —, aniline sulphite, I. 245*d*  
 —, aryl derivs., I. 245*c*  
 —, colour reactions, I. 244*d*  
 —, condensation with aromatic amines, I. 247*a*  
 —, — diamines, I. 246*c*  
 —, — hydroxylamine, I. 246*a*  
 —, — ketones, I. 247*d*  
 — dimethylamine sulphate, I. 245*d*  
 — hydrazones, I. 246*b*  
**Alloxanic acid**, I. 244*d*, 248*b*  
**Alloxan**, potassium, I. 245*b*  
**Alloxantin**, I. 248*b*, 249*d*  
 —, absorption spectrum, I. 248*d*  
**Alloxazine**, I. 246*d*  
 —, free radical from, I. 246*d*  
**Alloys**, see Alloys, light: Amalgam; Hume - Rothery's rule; and individual metals.  
 —, analysis, spectroscopic (see also Assaying; individual metals), II. 692*a*  
 —, electrodeposition, IV. 270*b*  
 —, light, I. 250*a*, 275*d*  
 —, plated, I. 258*a*  
**Allyl radical and compounds**, I. 256*a*  
 — acetate, I. 256*a*  
**Allylacetic acid**, I. 256*a*  
**Allylaceton**, I. 256*b*  
**Allylacetylene**, I. 256*b*  
**Allyl alcohol**, I. 256*b*  
**Allylamines**, I. 257*b*  
**Allylaniline**, I. 257*c*  
**Allylbenzene**, 3-methoxy-4-hydroxy-, IV. 394*c*  
**Allyl bromide**, I. 257*d*  
 — chloride, I. 257*d*  
 — cyanamide, I. 258*a*  
 — cyanide, I. 258*b*  
**Allylene**, I. 119*a*; II. 281*b*  
**Allyl ether**, I. 258*b*  
 — ethyl ether, I. 258*c*  
**Allylguaiacol**, IV. 395*b*  
**Allyl iodide**, I. 258*c*

**Allylmalonic acid**, I. 258*d*  
**Allyl mercaptan**, I. 258*d*  
 — mustard oil, I. 258*d*  
 — nitrite, I. 258*d*  
 — phenylthiourea, I. 250*a*  
 — polysulphides in garlic, V. 429*a*  
 — pyrrole, I. 250*a*  
 — sulphate, I. 259*a*  
 — sulphide, I. 259*a*  
 — isothiocyanate, I. 258*d*; III. 10*d*  
 — thiourea, I. 259*b*  
 — tribromide, I. 259*c*  
 — "Almalec," I. 277*a*  
**Almandine**, I. 259*c*; V. 429*c*  
 — "Almasium," I. 277*a*  
**Almond**, I. 259*c*  
 —, essential oil, I. 260*d*  
 — oil (fatty), I. 260*a*  
**Almonds**, sweet, enzyme from, IV. 283*b*  
**Alniresinol**, I. 198*a*  
**Alnulin**, I. 197*d*  
 — "Alocol," I. 261*b*  
**Aloe-emodin**, I. 261*b*  
 — fibres, I. 261*b*  
 — resins, I. 261*d*  
**Aloes**, bitter, I. 261*b*  
 — wood, I. 262*c*  
**Aloinose**, I. 154*a*  
**Aloins**, I. 261*d*, 262*d*  
 — "Aloxite," I. 4*a*, 262*d*  
 — glass-grinding stone, V. 598*d*  
**Alpaca**, I. 262*d*  
 — "Alpac," I. 251*b*, 262*d*, 277*c*  
**Alphanol dyes**, I. 262*d*  
 — "Alphogen," I. 262*d*; IV. 28*c*  
 — "Alphol," I. 262*d*; IV. 29*d*  
 — "Alphozone," I. 262*d*; IV. 28*c*  
**Alpinia** oil, A. *malaccensis*, I. 263*a*  
**Alquifou**, alquifoux, I. 263*a*; V. 415*c*  
 — "Aisil," IV. 248*c*  
 — "Alsol," I. 263*a*  
**Alstonia bark**, I. 263*a*  
**Alstonia spp.**, alkaloids, I. 263*a*  
**Alstonidine**, alstonine, I. 263*c*  
**Alstonite**, I. 263*d*, 613*b*, 638*a*  
 — "Altai," I. 263*d*  
**Althaea officinalis**, I. 263*d*  
 — *rosea*, I. 264*a*  
**Althæin**, althein, I. 264*a*; VI. 85*d*  
**Altrose**, I. 264*b*; II. 280*a*  
**Aludel**, I. 264*b*  
 — "Aludur," I. 277*a*  
**Alum**, ammonium, I. 200*c*  
 — "Alumatol," I. 264*c*  
**Alum**, burnt, I. 205*d*  
 — "Alum cake," I. 280*b*  
**Alum**, chrome, or chromium, III. 100*d*  
**Alumina**, I. 290*d*  
 — "Alumilite" protection of metals, III. 392*c*  
**Alumina** (see also Corundum; Gems, artificial), I. 281*a*  
 —, calcined or hydrated, for glass making, V. 501*c*  
 —, catalytic action on methane, II. 341*d*  
 — "Alumina hydrate," I. 290*d*  
**Alumina** production, I. 265*d*; II. 320*a*  
 — white, I. 290*d*  
**Aluminates**, I. 284*b*  
**Alumine** hydratée des Beaux, I. 656*c*

- Aluminite**, I. 264c, 289a  
**Aluminium**, I. 264c  
 — acetate, I. 292c  
 — acetylacetone, I. 293a  
 — action on phenol, II. 306d  
 — alkyl halides, I. 293b  
 — alkyls, I. 293a  
 — alloys (*see also* Alloys, light), I. 250a, 275d  
 — and chromium, analytical separation, VI. 299b  
 — as trace element, I. 504d, II. 496b  
 — borates, I. 291d  
 — borides, I. 291c; II. 30b  
 — borocarbide, I. 292a  
 — borotartarate, II. 30c  
 — brassy, bronzes, etc., I. 276d  
 — bromate, I. 288a  
 — bromide, I. 287d  
 — carbide, I. 291d; II. 281c  
 — —, formation, II. 360a  
 — carbonate, I. 292a  
 — carbonyl, I. 292a  
 — cerium alloy, II. 507d  
 — chemical properties, I. 273a  
 — chlorate, I. 287c  
 — chloride, I. 286d  
 — chloro-formate, I. 292c  
 — chlorosulphate, I. 291a  
 — citrate, I. 293a  
 — containing minerals, for glassmaking, V. 561c  
 — corrosion by inorganic substances, I. 273d, 274a  
 — —, organic substances, I. 274c  
 — —, prevention, I. 275a  
 — cyanamide, I. 292b  
 — cyanide, I. 292a  
 — —, detection and detn., I. 279b  
 — —, by micro-methods, I. 279d  
 — —, detn., assay, I. 521d  
 — —, colorimetric, I. 279c; II. 660d  
 — —, gravimetric, I. 279b; II. 591d  
 — —, in clay, III. 202c  
 — —, food, II. 650d; V. 292c  
 — —, volumetric, I. 279b; II. 650b  
 — dithionite, I. 291a  
 — drop reaction, II. 579c  
 — electrodeposition, IV. 270a  
 — electroplating on, I. 278d  
 — ethoxide, I. 28c, 293b  
 — fluoride, I. 285d  
 — foil, I. 278b  
 — formate, I. 292c  
 — gluconate in tanning, II. 297b  
 — higher oxides, I. 283c  
 — hydrogen compounds, I. 280c  
 — hydroxide, I. 283c  
 — — gels and sols, I. 283d  
 — —, mineral form, II. 25c  
 — hypochlorite, I. 287c  
 — industrial uses, I. 278b  
 — iodate, I. 288c  
 — iodide, I. 288a  
 — methoxide catalyst, II. 350d  
 — nitrate, I. 285b  
 — — acetate, I. 285c, 293a  
 — nitride, I. 284d  
 — nitrite, I. 285b  
 — oleate, I. 293c  
 — organic compounds, I. 292c  
 — oxalate, I. 293b  
 — oxide, I. 281a; IV. 175a  
 — paint, I. 278c  
 — palmitate, I. 283c; V. 195c  
 — perchlorate, I. 287c  
 — physical properties, I. 271d  
 — polishing, I. 278d  
 — powder, I. 278c  
 — production, carbon electrodes, I. 268d  
 — —, electrolytic, I. 265a, 269c  
 — —, reduction furnaces, I. 269c  
 — qualitative reactions, II. 548a, 552a, 568a; IV. 173d  
 — —, rare metals present, II. 550d  
 — selenate, I. 291b  
 — selenide, I. 291a  
 — selenite, I. 291a  
 — selenocyanate, I. 292c  
 — silicate, in building materials, II. 133b  
 — silicates, I. 291b  
 — stearate, I. 293d  
 — subchlorides, I. 286d  
 — subfluorides, I. 285d  
 — suboxides, I. 281a  
 — sulphate, I. 288d  
 — — acetate, I. 292d  
 — sulphide, I. 288c  
 — sulphite, I. 288d  
 — tartrate, I. 293d  
 — tellurate and telluride, I. 291b  
 — tellurite, I. 291b  
 — thiocyanate, I. 292b  
 — triisobutoxide, II. 170c  
 — triphenyl, I. 293b  
 — vessels in McOII synthesis, II. 350b  
**Alumino-ferric**, I. 289c  
**Aluminon**, I. 280a, 296d  
**Alum**, iron, I. 293d  
 — meal, I. 295b  
 — mineral, I. 261c, 291a  
 — "Alumnasol," I. 296d  
 — "Alumnol," I. 296d; IV. 30a  
**Alum**, potash, or potassium, I. 291a  
 — rock (*see also* Alunite), I. 294a  
**Alums**, I. 293d  
**Alum-shale**, I. 297a  
 — soda, or sodium, I. 296a  
 — stone (*see also* Alunite), I. 297d  
 — "Alundum," I. 297b, 657b; III. 399c  
**Alunite**, I. 264c, 294a, 297d  
**Alunogen**, I. 289a, 298c; IV. 591d  
**Alva**, I. 199a  
 — "Alvar," I. 90c, 94d  
**Alvite**, VI. 169a  
 — "Alypin," I. 298c, 369a  
**Amadou**, I. 298a  
**Amalgam**, I. 298d  
**Amalic acid**, I. 249c  
**Amandin**, I. 300d  
**Amanil dyes**, I. 300d  
**Amanita muscaria**, I. 300d  
**Amaranth**, I. 300d  
**Amarillite**, I. 300d  
**Amarine**, VI. 99a  
 —, luminescent oxidation, III. 24a  
 — "Amarin," I. 301a  
**Amatol**, I. 301a  
**Amatoxol**, I. 301d  
**Amazonite**, amazon-stone, I. 301c  
**Ambaline**, I. 301c  
**Ambari**, V. 164c  
**Ambatoarinite**, I. 370b  
**Amber**, I. 301d  
 — "Amber," I. 303a  
**Amber**, artificial, I. 302c, 614d  
 —, essential oil, I. 303a  
**Ambergris**, I. 303b  
**Amberite**, I. 303d  
**Ambler** gas analysis apparatus, II. 677a  
**Amblygonite**, I. 303d  
**Ambrein**, I. 304a  
**Ambrette**, I. 304a  
 — musk, I. 304b  
**Ambrettolide**, I. 304a  
 — "Ambrine," I. 304b  
**Ambrite**, I. 304b  
 — "Ambroid," I. 302b  
**Ambrosia artemisiifolia**, I. 304b  
 — "Ameisne," I. 304b  
**Ameliaroside**, VI. 93c  
 — "Ameryl," I. 304c  
 — "American Alloy," I. 253a, 277c  
**American ashes**, I. 304c  
 — "Ameroid," I. 304c  
**Amethyst** (dye), I. 305c, 576c  
 — (quartz), I. 304c  
 —, oriental, III. 308d  
**Amianthus** or amiantos, I. 304c, 499c  
**Amide powder**, I. 304c  
**Amides**, prepn., II. 371a, 375c  
 —, reduction, II. 374d  
**Amidine dyes**, I. 304d  
**Amidines**, I. 304d  
**Amidogène**, IV. 463a  
 — "Amidol," I. 305a  
 — "Amidopyrine," I. 305a  
**Amidoxyl benzoate**, I. 305b  
**Amines**, I. 305b  
 — aromatic, potentiometric detn., II. 707a  
 —, catalytic prepn., II. 128d  
 —, formation, II. 377b  
 —, physical properties, I. 310, 311  
 —, primary, detn., II. 627b  
 —, reactions, I. 312a  
**Aminoacetic acid**, VI. 71d  
 — acids, benzyl esters, VI. 72d  
**Amino-acids**, I. 316d  
 — acyl derivs., I. 319d  
 — esters, I. 319a  
 — of rice proteins, II. 493c  
 —, reagent for, I. 324b  
 —, salts, I. 319a  
 —, synthesis, II. 369d  
**Aminochrysenes**, dyes from, III. 118d  
 — "Aminoform," I. 326a  
**Aminoformic acid**, II. 278b  
**Aminolysis**, I. 322a; IV. 349d  
**Aminopeptidase**, IV. 325a  
 — "Aminophyllin," I. 326a  
**Amines**, I. 284d, 326a; III. 327d, 334a  
**Ammodendrine**, I. 326b  
**Ammolin**, II. 29d  
**Ammonal**, I. 326b  
**Ammon**, carbonit, IV. 554d  
**Ammonia**, I. 326d  
 —, absorption in sulphuric acid, I. 346d  
 —, aqueous solution, I. 328c, 330a

- Ammoniacal** liquor distillation, I. 344*d*  
 —, phenol from, II. 303*d*  
**Ammonia**, catalytic oxidation, II. 424*b*  
 —, cracked, for hydrogen supply, I. 330*d*; VI. 335*a*  
 — crackers, VI. 335*a*  
**Ammoniacum**, I. 356*c*  
**Ammonia**, detn., gravimetric, II. 598*c*  
 —, — in gases, II. 681*d*  
 —, —, —, micro-method, II. 681*b*  
 —, —, volumetric, II. 645*a*  
 — from blast-furnace gas, peat and shale, I. 342*a*  
 — coal-, lignite- or producer-gas, I. 338*d*  
 — in fire extinguishers, II. 350*c*  
 — liquid, as solvent, I. 331*b*  
 — production, I. 331*c*, 335*b*  
 —, qualitative reactions, II. 553*d*, 572*c*  
 — recovery as liquor or sulphate, I. 349*a*, 350*a*  
 —, —, direct and semi-direct processes, I. 340*b*; III. 262*b*; V. 461*a*  
 — from coke-oven gas, III. 265*a*  
 —, indirect process, I. 340*b*; V. 459*a*, 461*a*  
 —, Lynn or Power Gas Corp'n. system, V. 375*b*  
 —, Mond system, V. 374*c*  
 — soda process, II. 326*a*  
 — synthesis, I. 331*c*, 335*b*  
 —, American processes, I. 338*a*  
 —, catalysts, I. 333*d*  
 —, direct, I. 332*a*; II. 423*d*  
 —, hydrogen production for, (see also Hydrogen production), I. 334*c*; VI. 333*d*  
 —, theoretical basis, II. 534*c*  
 —, technical, as liquor and anhydrous liquid, I. 350*c*  
**Ammoniated** superphosphate, I. 353*d*  
**Ammonite**, IV. 554*a*  
**Ammonium** bicarbonate, I. 351*d*  
 — borate, occurrence, II. 35*b*  
 — calcium ferrocyanide, III. 470*d*  
 — carbonate, I. 351*c*; II. 278*b*  
 — carbonate, I. 351*c*  
 — chloride, I. 351*d*  
 —, —, vapour density of dry, IV. 80*b*  
 — chromate, III. 111*c*  
 — cyanate, III. 507*a*  
 — dichromate, III. 111*c*  
 — ferrocyanide, III. 470*c*  
 — ferrous ferrocyanide, III. 471*c*  
 — nitrate, I. 352*c*, 354*a*; IV. 464*a*  
 — N - nitrosophenylhydroxylamine reagent, II. 583*b*  
 — persulphate in flour, II. 81*d*  
 — phosphate, I. 352*d*  
 —, —, mono-, V. 223*a*  
 —, qualitative reactions, II. 553*d*, 572*c*  
 — salts, I. 331*a*, 350*d*  
 — in candle wicks, II. 265*a*  
 — sulphamate, flameproofing with, V. 198*c*  
**Ammonium** sulphate from coke-oven gas, III. 268*b*  
 — — gas liquor, I. 347*c*  
 — — gypsum, I. 351*a*  
 —, —, production, I. 342*a*, 350*d*; II. 424*b*  
 — thiocyanate, III. 508*d*; VI. 143*a*  
**Ammonolysis**, VI. 307*a*  
**Ammonpulver**, I. 357*a*  
**Amorphous**, I. 353*d*  
**Amolonia**, VI. 85*d*  
**Amosite**, I. 500*b*  
**Ampangabeite**, I. 357*b*  
**Ampelopsin**, I. 357*b*; IV. 554*c*  
 "Amphetamine," IV. 318*a*  
**Amphibole-asbestos**, I. 496*c*  
 "Amphotropin," I. 357*d*  
**Amyridaine** hydrochloride, I. 298*c*, 369*a*  
**Amygdalase**, II. 442*c*; IV. 282*d*  
**Amygdalin**, I. 250*c*, 260*b*, 357*d*  
 —, gentiobiose in, II. 299*b*  
**isoAmygdalin**, VI. 85*d*  
 "Amygdophenin," I. 358*a*  
**isoAmylacetate**, I. 36*a*  
**Amyl acetate**, in film dopes, II. 448*b*  
 — in lacquers, II. 469*a*  
 —, —, production, II. 471*d*  
 —, specifications, II. 472*b*  
**isoAmylacetate** acid, VI. 205*b*  
**isoAmylacetate** acid, ethyl ester, I. 61*c*  
**Amyl alcohol** as stabiliser, IV. 521*c*  
 — production (see also Fusel oil), I. 178*b*, 390*a*; II. 471*d*  
 — alcohols, I. 358*b*  
**n-Amylamine**, I. 361*b*  
**isoAmylamine** in ergot, IV. 331*d*  
**Amylan**,  $\alpha$ - and  $\beta$ -, I. 363*a*  
**Amyl** and amylic compounds, I. 358*a*  
**Amylarine**, I. 363*c*  
**Amylase** (see also Diastase; Brewing), I. 363*c*; II. 302*c*; IV. 311*d*, 313*b*; VI. 305*b*, 390*d*  
 —,  $\alpha$ - and  $\beta$ -, in brewing, II. 88*a*  
 — in millet, II. 480*b*  
 — rice, II. 495*b*  
**Amyl bromide**, I. 361*b*  
**isoAmylcupreine**, III. 161*c*  
**Amylenes**, I. 361*d*, 364*b*  
**Amylenol**, I. 362*d*  
**Amyl esters**, I. 361, 362*d*  
 — ether, I. 362*a*  
 — fluorides, I. 362*a*  
**isoAmylformal**, I. 34*b*  
**isoAmylhydrocupreine**, III. 168*b*  
**isoAmylhydrocupreine** hydrochloridium, IV. 392*c*  
**Amylobacter pectinovorum**, V. 159*c*  
**Amylodextrins**, II. 88*a*, 298*d*; III. 567*d*, 568*a*  
 "Amyloform," I. 365*a*  
**Amylokinase**, II. 88*a*  
**Amylopectin**, I. 365*a*  
 — in rice, II. 494*c*  
**Amylopsin**, I. 890*b*  
**Amylose**, I. 365*a*  
**Amylosynthase**, II. 495*c*  
**2-n-Amylquinoline**, 4-methoxy-, III. 402*d*, 463*a*  
**isoAmyltrimethyl-ammonium** hydroxide, I. 363*c*  
**Amyrilene** in cacao butter, II. 185*d*  
**Amyrins**,  $\alpha$ - and  $\beta$ -, I. 365*c*; IV. 275*c*  
 "Amytal," I. 365*d*, 368*b*, 623*a*  
**Anabesine**, I. 365*d*  
 "Anacardic acid," I. 366*a*  
**Anacardium** nut, *A. occidentale*, I. 12*b*, 365*d*  
 "Anæsthesine or "Anæsthesine," I. 366*b*, 369*b*, 371*c*  
**Anæsthetic** acetylene, I. 367*c*  
 — chloroform, I. 367*c*; III. 70*b*  
 — "Chloryl," IV. 350*a*  
 — divinyl ether, I. 368*a*  
 — ether, I. 367*b*; IV. 380*d*, 388*a*  
 — ethers, comparison of, IV. 353*c*  
 — ethyl chloride, I. 367*b*  
 — ethylene, I. 367*d*; VI. 373*a*  
 — nitrous oxide, I. 367*a*  
**Anæsthetics**, I. 366*b*  
 —, explosion risks with, I. 368*a*; IV. 388*a*, 427*c*  
 —, local, I. 368*c*  
**Anagyris**, *Anagyris foetida*, I. 369*d*  
 "Anahæmin," VI. 204*d*  
 "Analgen," I. 369*d*  
**Analgesine**, I. 369*d*  
 "Analutol," I. 370*a*  
**Analysis**, absorption spectra in, II. 709*a*  
 —, azeotropes in, II. 711*a*  
 —, chemical (see also Assaying), II. 541*b*  
 —, chromatographic, II. 628*a*; IV. 174*c*  
 —, combustion, of carbon compounds, II. 615*a*  
 —, —, micro-method, II. 630*c*  
 —, drop reactions, II. 579*c*  
 —, electrochemical, conductivity methods, II. 692*b*  
 —, —, inner electrolysis in, II. 690*c*  
 —, —, micro-method, II. 690*c*  
 —, electrodeposition methods, II. 695*c*  
 —, electro-, Thiedebrand's method, II. 699*d*  
 —, gas, II. 674*d*, 687*d*  
 —, gravimetric, II. 582*c*  
 —, —, with cupferron, II. 583*b*  
 —, —, oxine, II. 583*b*  
 —, —, quinaldine acid, II. 583*c*  
 —, hydrogenation, macro- and micro-, VI. 359*b*  
 —, micro-, detn. of organic radicals, II. 633*d*  
 —, —, gas, II. 680*d*  
 —, —, gravimetric methods, II. 620*b*  
 —, —, volumetric methods, II. 633*d*  
 — of carbon compounds, tests for elements, II. 615*a*  
 — dyes, IV. 174*c*, 194*d*, 239*a*  
 —, polarographic, II. 710*b*  
 —, potentiometric, II. 702*d*  
 —, proximate, of carbon compounds, II. 623*b*

- Analysis**, qualitative (*see also* Borax beads; Cobalt nitrate reactions; Flame colorations; Microcosmic salt beads; "Silica skeleton test"), II. 545*d*  
 —, dry tests, II. 547*a*, 548*b*  
 —, groups I and II, II. 551*a, c*  
 —, group III (phosphates absent), II. 552*a*  
 —, — (phosphates present), II. 552*a, b*  
 —, —, IV. II. 552*b*  
 —, —, V. II. 553*a*  
 —, —, VI. II. 554*a*  
 —, open tube method, II. 547*b*  
 —, rare metals absent, II. 550*c*  
 —, — present, II. 554*a*, 550*d*  
 —, solvent action of mineral acid, II. 540*b*  
 —, quantitative, II. 582*c*  
 —, reactions of organic acids, II. 550*a*  
 —, rare earth metals, II. 550*c*  
 —, special reactions, II. 555*d*  
 —, spectrum, *see* Spectrum analysis.  
 —, "spot" tests, *see* Drop reactions.  
 —, titration, conductivity method, II. 603*d*  
 —, ultimate, of carbon compounds, II. 615*a*  
 —, volumetric, II. 634*d*  
 —, calibration of vessels, II. 635*c*  
 —, detn. of combined acids, II. 646*b*  
 —, — free acid in salts, II. 646*b*  
 —, iodine, thiosulphate and arsenite methods, II. 648*b*  
 —, of acids, II. 645*a*  
 —, alkaline substances, II. 644*a*  
 —, standard solutions, II. 641*c*  
 —, with ceric sulphate, II. 647*d*  
 —, — dichromate, II. 647*b*  
 —, — permanganate, II. 648*c*  
 —, — silver nitrate, II. 649*c*  
 —, — stannous chloride, II. 649*b*  
 —, — titanous chloride, II. 649*a*; IV. 239*a*  
*Anamirta paniculata* (*see also* *Cocculus indicus*), I. 370*a*  
**Anamirtin**, I. 370*a*  
*Ananas sativus*, I. 458*d*  
**Anatase**, I. 370*a*  
 "Anayodin," I. 370*a*  
**Ancylite**, I. 370*a*  
**Andalusite**, I. 264*d*, 370*b*  
**Andeer's** lotion, IV. 29*c*  
**Andesine**, I. 370*c*  
**Andesite**, I. 370*c*  
**Andiroba** oil, II. 277*b*  
**Andorite**, I. 370*d*  
**Andradite**, V. 429*b*  
**Andropogon** oils\* (*see also* Citronella), III. 183*d*  
**Androsin**, I. 370*d*; VI. 85*d*  
**Androstan-3-ol-17-one**, I. 370*d*  
**Δ<sup>14</sup>-Androsten-3-one-17-ol**, I. 371*a*  
**Androsterone**, *cis*-androsterone, I. 370*d*, VI. 274*d*  
**Anemolic acid**, I. 371*b*  
**Anemonin**, anemoninic acid, I. 371*b*  
 "Anesin" or "Aneson," *see* Acetone-chloroform.  
 "Anesthesine" or "Anesthesine," I. 366*b*, 369*b*, 371*c*  
 "Anestile," IV. 359*a*  
**Anethole**, I. 371*c*  
**Anethum graveolens**, I. 371*c*; IV. 4*c*  
**Aneurin**, I. 371*c*, 583*b*; VI. 138*d*  
**Angel** electrolytic cell, III. 68*a*  
**Angelica**, essential oil, I. 371*c*  
**Angeline**, I. 371*d*  
**Anglesite**, I. 371*d*  
 "Anglopyrin," I. 517*d*  
**Angostura** or **Angustura** bark (*see also* *Cusparia* bark), III. 462*b*  
**Angosturin** and **angosturine**, III. 463*a, c*  
**Angular** leaf spot, V. 139*a*  
**Anhaline**, I. 371*d*; VI. 260*a*  
**Anhydrides**, acid, preparation, II. 370*b*  
**Anhydrite**, I. 372*a*; II. 129*b*, 130*a*  
 —, conversion into ammonium sulphate, II. 424*b*  
 "Anhydrite, insoluble" and "soluble," II. 130*a*  
**Anhydroazafurinoneamide**, II. 395*d*  
**Anhydrobrazilic acid**, II. 69*d*  
**Anhydrocapsanthrone**, II. 273*a*  
**Anhydrogitalin**, II. 384*b*  
**Anhydron**, III. 68*d*  
**Anhydro-osazonones**, II. 293*b*  
**Anhydropermonosulphuric acid**, II. 393*d*  
**Anilic acids**, preparation, II. 371*b*  
**Anilides**, preparation, II. 371*b*  
**Aniline**, I. 372*c*  
 — Blue, -Brown, -Red, -Scarlet, I. 376*d*  
 — from phenol, II. 307*a*  
 — nitrite, III. 581*a*  
 —, *o*- and *p*-nitro-, I. 39*a*  
 —, pyrolysis, II. 278*c*  
 —, tetranitro-, IV. 487*d*  
**β-Anilinobutaldehyde** ethyl-acetal, I. 36*b*  
**Anilinobutylideneaniline**, I. 29*d*  
**Animal oil**, II. 29*c*; VI. 135*b*, 280*d*  
 —, Dippel's oil, II. 29*c*  
**Animé** or **Animi**, *see* Elemi.  
**Animin**, II. 29*d*  
**Anion acids**, VI. 247*a*  
**Anisaldehyde**, I. 376*d*  
**Aniseed**, I. 376*d*  
**Anise oil**, I. 377*a*  
**Anisic acid**, I. 377*a*  
**Anisidine**, *o*-, *m*-, and *p*-, I. 377*b*  
**Anisole**, I. 377*d*  
 —, *s*-trinitro-, IV. 484*a*  
**Ankerite**, I. 378*a*; IV. 53*d*  
 "Annaline," VI. 160*c*  
**Annatto**, I. 378*a*  
**Annealing**, I. 379*a*  
 —, bright, VI. 334*c*  
**Annivite**, IV. 590*d*  
**Anodic** efficiency, IV. 261*c*  
**Anodic** oxidation of metals III. 392*b*; IV. 271*d*  
**Anodising**, IV. 271*d*  
**Anodynine**, *see* Antipyrine.  
 "Anogon," I. 380*d*  
 "Anol," VI. 225*d*  
 "Anon," I. 380*d*  
**Anorthite**, I. 264*d*; II. 228*c*; V. 1*d*  
**Anserine**, I. 380*d*; II. 392*a*  
**Antalgine** (*see also* *Agathum*), I. 381*a*  
**Anthanthrone**, I. 426*a*  
**Anthemene**, anthemol, I. 381*a*  
*Anthemis nobilis*, essential oil, I. 381*a*; II. 520*a*  
**Anthraxanthin**, I. 381*a*; II. 390*d*  
**Anthocyanidins**, I. 381*b*  
**Anthocyanins**, I. 318*b*; II. 120*b*, 183*b*, 234*b*  
 —, sugar in, II. 299*b*  
**Anthocyan**, I. 381*b*  
**Anthophyllite**, I. 490*c*  
**Anthorine**, *ψ*-anthorine, I. 124*a*  
**Anthracene**, I. 382*a*  
 —, additive compounds, I. 385*c*  
 —, detn., I. 386*d*  
 — from anthraquinone, I. 388*b*  
 —, halogenation, I. 386*b*  
 —, hydrogenation, I. 386*c*; VI. 352*d*  
 oil, I. 126*b*; III. 208*b*, 211*c*  
 —, in wood preservation, II. 308*d*  
 —, oxidation, II. 128*a*  
**Anthrachrome** dyes, I. 387*c*  
**Anthrachrysazin**, *see* Anthrachrysone.  
**Anthrachrysone** or **anthrachrysazin**, I. 213*a*, 226*c*, 405*a*  
 -2:6-disulphonate, I. 392*d*  
**Anthracite**, V. 344*a*  
**Anthraflavic acid**, *see* Anthraflavin.  
*iso*Anthraflavic acid, I. 212*d*  
**Anthraflavin**, I. 206*a*, 212*d*, 223*a*, 402*c*  
*iso*Anthraflavin, I. 206*a*, 212*d*, 223*b*  
**Anthraflavin**, 1:5-dinitro-, I. 392*c*  
 — 3:7-disulphonic acid, I. 390*b*, 392*d*  
*iso*Anthraflavin, 1:3:6:8-tetra-nitro-, I. 392*d*  
 — 3:6-disulphonic acid, I. 390*b*, 392*d*  
**Anthraflavone** G, I. 418*d*  
**Anthrafuchson**, I. 431*c*  
**Anthragallol**, I. 212*d*, 223*b*, 402*c*  
**Anthragallolamide**, I. 223*d*  
**Anthragallol**,  $\alpha$ - and  $\beta$ -hydroxy-, I. 212*d*, 226*a*  
 —, dihydroxy-, I. 212*d*, 227*b*  
 — 1:2- and 1:3-dimethyl ethers, I. 223*d*; II. 524*a*  
 —, 4-nitro-, I. 392*d*  
**Anthrahydroquinone**, 1:2-dihydroxy-, I. 219*d*  
**Anthrahydroquinones**, I. 215*a*  
**Anthralan** colours, I. 407*d*

- Anthranol**, I. 215a, 388b, **430a** ;  
 II. 410d  
 —, dihydroxy-, III. 127d  
 —, 1:2-dihydroxy-, I. 219d  
**Anthrapinacene**, I. 432b  
**Anthrapurpurin**, I. 200a, 212d, 225a  
**Anthrapurpurinamide**, I. 225c  
**Anthrapurpurin**, hydroxy-, I. 213a  
**Anthraquinol**, I. 388b, 430d  
**Anthraquinone**, I. 200c, 207a, 387d, 505a  
 —, acylamino-, vat dyes, I. 205c  
 —, acyl derivs., I. 396d  
 —, alkyl derivs., I. 395c  
 —, alkyloxy derivs., I. 211b  
 —, 1- and 2-amino-, I. 206a, 211c, 394c, 412b  
 —, 1-amino-2:3-dihydroxy-, I. 223d  
 —, 1-amino-2:4-dinitro-, I. 392a  
 —, 2-amino-3-nitro-, I. 392a  
 —, 6-amino-1:2:5:8-tetrahydroxy-, I. 228c  
 —, aroyl derivs., I. 396d  
 —, aryl derivs., I. 395c  
 —, 2-chloro-, I. 208b, 210d, 402c  
 —, chloro-derivs., I. 397d  
 —, 1-chloro-4-hydroxy-, I. 402c  
 —, 1-chloro-4-nitro-, I. 392b  
 —, colours, brilliancy, I. 429c  
 —, derivs., replacement actions, I. 211a  
 —, **N**:**N'**-dibenzoyl-1:5-diamino-, I. 232d  
 —, dichloro-, I. 211a, 402c  
 —, 2:4-dichloro-1-amino-, I. 207d  
 —, 1:5-dichloro-4:8-dinitro-, I. 392b  
 —, 1:8-dichloro-4:5-dinitro-, I. 392b  
 —, 1:8-dichloro-4-nitro-, I. 392b  
 —, dichloro-, disulphonic acids, I. 390d  
 —, —, monosulphonic acids, I. 390d  
 —, 1:2-dihydroxy- (see also Alizarin; Alizarin and allied dyes), I. 397d, 402c; II. 523d  
 —, 1:3-dihydroxy-, I. 220c  
 —, 1:3-dihydroxy-4-amino-, I. 224b  
 —, 1:4-dihydroxy-, I. 220d  
 —, 1:5-dihydroxy-, I. 221d  
 —, 1:6-dihydroxy-, I. 222a  
 —, 1:7-dihydroxy-, I. 222b  
 —, 1:8-dihydroxy-, anthranol, III. 120c  
 —, 2:3-dihydroxy-, I. 222c  
 —, 2:6-dihydroxy-, I. 223a  
 —, 1:5-dinitro-, I. 206a, c; 210d, 391a  
 —, 1:8-dinitro-, I. 210d, 391a  
 —, 2:7-dinitro-, complex with chrysene, III. 118c  
 —, disulphonic acids, I. 208d, 200c, 210c  
 —, 2:6-disulphonic acid, 1:5-dihydroxy-4:8-diamino-, I. 206d  
 —, 3:7-disulphonic acid, 1:2:4:5:6:8-hexahydroxy-, I. 206d  
 —, dyes (see also Alizarin and allied dyes; Dyeing; Vat dyes), I. 402d  
**Anthraquinone** from phthalic anhydride and benzene, I. 101d  
 —, 1:2:3:5:6:7-hexahydroxy-, I. 227c  
 —, 1:2:4:5:6:8-hexahydroxy-, I. 227c  
 —, 1:2:1:5:7:8-hexahydroxy-, I. 227c  
 —, 1-hydroxy-, I. 216a  
 —, 2-hydroxy-, I. 216b, 402c; II. 524c  
 —, 1-hydroxy-4-benzoylamino-, I. 206d  
 —, 1-hydroxymethyl-1:8-dihydroxy-, I. 261b  
 —, leuco-1:4-diamino-, I. 409b  
 —, 1-nitro-, I. 206c, 210d  
 —, 1-nitro-, 5-and-8-sulphonic acids, I. 391d  
 —, 3-nitro-1:2:1:5:7:8-hexahydroxy-, I. 228b  
 —, nuclear syntheses, I. 400d  
 —, 1:2:3:5:7-pentahydroxy-, I. 227b  
 —, 1:2:4:5:8-pentahydroxy-, I. 227b  
 —, phenoxv-derivs., I. 211b  
 —, production, II. 428a  
**Anthraquinones**, acylamino-, I. 206d  
**Anthraquinone**, 1-saheyl-amino-, I. 233a  
**Anthraquinones**, amino-, I. 205c, 211c, 391c, 111b  
 —, —, halogenation, I. 397b  
 —, diamino-, I. 212a, 392b, 395a  
 —, dihydroxy-, I. 220c, 221d, 222, 223, 397d  
 —, hydroxy-, I. 203b, 212d, 397d  
 —, —, constitution, I. 215c  
 —, —, lakes from, and properties, I. 215d, 216a  
 —, —, reduction, I. 215a  
**Anthraquinone-1-** (or  $\alpha$ -) sulphonic acid, I. 209b  
 —, 2- (or  $\beta$ -) sulphonic acid, I. 210a  
 —, sulphonic acids, I. 208d  
 —, 1:4:5:8-tetra-amino-, I. 212b  
 —, 4<sup>2</sup>-tetrahydro-, I. 208b  
 —, 1:2:3:1-tetrahydroxy-, I. 220a  
 —, 1:2:5:6-tetrahydroxy-, I. 220b  
 —, 1:2:5:8-tetrahydroxy-, I. 226b  
 —, 1:3:5:7-tetrahydroxy-, I. 226c  
 —, 1:4:5:8-tetrahydroxy-, I. 227a  
 —, thioglycollic acid dyes, I. 232c  
 —, 1:4:6-trichloro-, I. 402c  
 —, 2:3:6-trichloro-, I. 402c  
 —, 1:2:3-trihydroxy-, I. 223c  
 —, 1:2:4-trihydroxy-, I. 223d  
 —, 1:2:5-trihydroxy-, I. 224c  
 —, 1:2:6-trihydroxy-, I. 224c  
 —, 1:2:7-trihydroxy-, I. 225a  
 —, 1:2:8-trihydroxy-, I. 225d  
 —, 1:3:8-trihydroxy-, I. 212d, 225d  
 —, 1:4:6-trihydroxy-, I. 212d, 225d  
 —, 1:4:8-trihydroxy-, I. 212d  
**Anthraquino-quinolines**, I. 396d  
**Anthrarobin**, I. 219d, 433a; III. 117d  
**Anthra Rubine R**, I. 415c  
**Anthrarufin**, I. 221d  
 —, as intermediate, I. 405a  
 —, diacetyl-, I. 222a  
 —, 4:8-diamino-, I. 205c, 212c  
 —, 4:8-dinitro-, I. 212d, 392c  
 —, 2:6-disulphonic acid, I. 390b, 392d  
 —, hydroxy-, I. 200a, 212d, 224c  
 —, synthesis and prepn. I. 212d, 221d  
 —, 2:1:6:8-tetranitro-, I. 392c  
 —, 2:1:6:8-tetrasulphonic acid, I. 390b  
**Anthrimides**, I. 411b  
**Anthrone**, I. 206c, 215a, 388b  
 —, 1-chloro-, I. 432d  
 —, derivs., I. 432d  
 —, prepn., I. 430a  
**Anti-agers** for rubber, I. 29d  
**Antiarigenin**, II. 387c  
**Antiarin**,  $\alpha$ - and  $\beta$ -, I. 433a; II. 387c; VI. 86a  
**Antiarose**, II. 387c  
**Anti-catalysts**, see also Catalyst poisons.  
 —, in drying oil, IV. 92a  
 —, prepn. of bornyl chloride, II. 251b  
**Anti-chlor**, I. 433b  
**Anticoagulants**, blood, II. 24b  
**"Anticol,"** I. 433b  
**"Anticorodal,"** I. 253a, 277a  
**Anti-corrosion**, III. 385c  
**Anti-dimming** materials in respirators, III. 18d  
**"Antidin,"** I. 433b  
**"Antifebrin,"** I. 38d, 133b  
**Anti-flash** compounds, IV. 521d  
**"Antiformin,"** I. 433b  
**Anti-fouling** paints, III. 383c  
**Anti-friction** metal, I. 446a  
**Anti-froths**, V. 280a  
**"Antifungin,"** I. 433b  
**Antigen** of blood, II. 22b  
**Antihypo**, I. 433b  
**Anti-knock** addition to petrol, I. 674a; IV. 417d, 449a  
 —, —, agents, metal carbonyls as, II. 358d  
**"Antileprol,"** I. 433c  
**"Antileutin,"** I. 433c  
**Antimonial**, aliphatic, I. 434a  
 —, alkyl, dihalides, I. 434b  
 —, aromatic, I. 435c  
 —, cyclic, I. 437c  
 —, detn. of antimony in, II. 622b  
 —, organic, I. 433c  
**Antimonine**, I. 439c  
**Antimonious** oxide, I. 448a  
 —, pigment, I. 449c  
**Antimonite**, I. 439c, d  
**Antimony**, I. 439c  
 —, blends, I. 439d  
 —, bloom, I. 439d  
 —, Butter of, I. 417d  
 —, cacodyl, I. 431c  
 —, chloride as chlorine carrier, II. 353b  
 —, chromium alloy, III. 104a  
 —, cinnabar, I. 447c; II. 233d  
 —, crocus, I. 447b  
**"Antimony, crude,"** I. 442a, 446b

- Antimony**, detn., assay, I. 522a  
 —, —, colorimetric, II. 670c  
 —, —, electrodeposition method, II. 700a  
 —, —, gravimetric, II. 600b  
 —, —, in enamelled ware, V. 202d  
 —, —, iodimetric, II. 651c  
 —, —, potentiometric, II. 707a  
 —, drop reaction, II. 579d  
 —, glance, I. 439d  
**Antimonyl** compounds, I. 438d  
**Antimony**, luminescent reaction, III. 23d  
 — mordant, I. 448c  
 —, nickeliferous grey, I. 439d  
 — ore, I. 446b  
 — oxide as catalyst, II. 350d  
 —, —, complexes with catechol, II. 431a  
 —, —, for glassmaking, V. 500a  
 — oxychloride, I. 448a  
 — pentachloride, chlorination catalyst, II. 428d  
 — pentafluoride, I. 448c  
 — pentasulphide, I. 447a  
 —, qualitative reactions, II. 551d, 573d  
 —, —, rare metals present, II. 551d, 556d  
 — saffron, I. 447b  
 — salt or salts, I. 448b, d  
 — sesquisulphide, I. 440b  
 — tetroxide, I. 448b  
 — trichloride, I. 447d  
 —, —, reaction with carotene, II. 394d  
 — trifluoride, I. 448c  
 — trioxide, I. 448a  
 — trisulphide, I. 440b  
 "Antinonin," I. 448; IV. 30c  
 "Antinosin," I. 448d  
**Anti-oxidants** (see also Inhibitors, gum), VI. 468d  
 —, —, addition to benzole motor fuel, I. 674b  
 —, —, for drying oils and rubber, II. 427c; IV. 02a  
 —, —, in food, II. 427c; V. 306a  
 "Antiperiodyin," "Antiperioslin," I. 449a  
 "Antipyrin" I. 369d, 449c; VI. 300d, 302b  
**Antipyrine**, 4-dimethylanilino-, I. 305a  
**Antirrhinin**, I. 449a  
**Antiseptics** (see also Disinfectants; Food preservatives).  
 —, acridine, I. 133d  
 —, benzoic acid, IV. 28c; V. 300c  
 —, butyric acid, IV. 28b  
 —, camphor, IV. 30d  
 —, carbon tetrachloride, IV. 30d  
 —, cinnamic acid, IV. 29a  
 —, creosol, IV. 29c  
 —, creosote, III. 420a, 422a; IV. 29d  
 —, cresols, IV. 29b  
 —, cresylic acid, III. 427d  
 —, essential oils, IV. 30d  
 —, halogenated aromatic compounds, IV. 30c  
 —, hops, II. 92a  
 —, hydrocarbon, IV. 30c  
 —, lanolin, III. 92c  
 —, lysol, III. 427d  
 —, nitro-compounds, aromatic, IV. 30c  
**Antiseptics**, perborates in, II. 52a  
 —, petroleum, IV. 30c  
 "Antitussin," I. 449c  
**Antivenenes**, antivenom sera, II. 24d  
 "Antodyne," I. 449c  
 "Antox," I. 449c  
**Aomai**, II. 495d  
**Apallagin**, I. 449c  
**Apatite**, I. 449c; II. 204a, 224c  
 — for superphosphate manufacture, V. 68c  
 — in bone, II. 27c  
**Aphis sinensis**, V. 426c  
**Aphthalite**, I. 450b  
**Aphylline**, I. 365d  
**Apigenin**, II. 520b; V. 514b; VI. 171c  
**Apigeninidin**, 5-glucosidyl-, V. 529d  
**A.P.I.** gravity scale, I. 450c  
**Apiin**, I. 450c; II. 288d; V. 514b  
 — in celery, II. 441b  
 —, methoxy-, VI. 92a  
**Apionic acid**, I. 450d  
**Apiose**, I. 450c; II. 288d  
**Apis spp.**, V. 530b; VI. 262d, 263b  
**Apium petroselinum**, I. 450d  
**Apilite**, VI. 126b  
**cisApocamphoric acid**, II. 34b  
**Apocarnitine**, I. 450d; II. 391c  
**Apocholic acid**, compound with camphor, II. 210d  
**Apocinchene**, III. 111a  
**Apocinchonidine**, III. 153c  
**Apocinchonine**, III. 157a  
**Apocyclene**, II. 240c  
 "Apolysin," I. 450d  
**Apomorphine methyl bromide**, II. 118d; IV. 401d  
 "Aponal," I. 450d  
**Apoposphorylase**, V. 35c  
**Apophyllite**, II. 227c  
**Apoquinamine**, III. 169a  
**Apoquinene**, III. 141a, 178a  
**Apoquinidine**, III. 149c, 171b  
**Apoquinine**, III. 149c, 170b  
**Aporeine**, I. 450d  
**Aporphine alkaloids** (see also isoQuinolone alkaloids), III. 400b  
**Aposafranines**, I. 570c, 575c  
**Aposafranone**, I. 571a  
 "Apothesine," I. 369a, 451a  
**Apozymase**, III. 250c  
**Apple**, I. 451a  
 — jack, I. 452b  
 — pulp, I. 452b; III. 124d  
**Apples**, cider, III. 122a  
**Apricot**, I. 452d  
 "Apyron," I. 453b  
 "Aquadag," I. 119d; II. 310b; III. 288a  
**Aquamarine**, I. 685b  
**Aqua regia**, solvent in analysis, I. 453b; II. 549d  
**Aquaresin G.M.**, I. 453c  
**Aquilin**, I. 136a  
**Araban**, II. 287a, 402c; VI. 155d  
**Arabic acid**, I. 12a; VI. 150b  
**Arabin**, I. 12a  
**Arabinogalacturonic acid**, II. 298a  
**Arabinose**, I. 453c; II. 282b  
**Arabitol**, I. 454a  
**l-Arabinonic acid**, I. 453d  
**Arachidic acid**, I. 454b, 456a  
 —, crude, I. 456b  
**Arachidonic acid**, III. 247b  
**Arachin**, I. 454c  
**Arachis hypogaea**, I. 454c; VI. 138a, 201c  
**Arachis oil**, I. 454c  
 "Arachlor," IV. 11a  
**Arachnoidiscus Ehrenbergii**, I. 163c  
**Aragonite**, I. 456d; II. 203b, 220b  
**Aralia spp.**, I. 457; VI. 80a  
**Aralligenin**, I. 457a  
**Aralin**, VI. 80a  
**Aramayoite**, I. 457b  
**Arandisite**, I. 457b  
 "Arappo," I. 653d  
**Arariba rubra**, I. 466b; VI. 188a  
**Araroba**, I. 457b; III. 116b  
**Ararobinol**, III. 118c, 117b  
**Arbotrine**, I. 457c  
**Arbutin**, I. 457c; VI. 86a  
 —, monobenzoyle, II. 443b  
**Arbutus ura-ura**, I. 457c  
**Arcaine**, I. 457c  
**Arcanite**, I. 450b  
**Arca noa** (mollusc), I. 457c  
**Archangelica officinalis**, I. 371c  
 "Archibromin," I. 457d  
**Archil** substitute, IV. 207a  
 "Archiodin," I. 457d  
**Arctic sperm oil**, II. 53d  
**Arctostaphylos ura-ura**, I. 660b; IV. 333b  
**Ardennite**, I. 457d  
**Areca catechu**, I. 458a  
**Arecaine**, I. 458a  
**Arecaine**, I. 458a  
**Areca nut**, I. 458a  
**Arecolidine**, I. 458a  
**Arecoline**, I. 458a  
**Arenobufotoxin**, II. 388b  
**Areometer**, Cartier's, I. 188c  
**Argal** or Argol, I. 461d  
**Arganine**, I. 458b  
**Argan oil**, I. 458b  
 "Argentamine," I. 458c; IV. 26a  
**Argentine**, I. 458c  
**Argentite**, I. 458c; VI. 206a  
**Argan fibre**, I. 458d  
**Arginase**, I. 458d, 461c  
**Arginine**, di- and L-, I. 459b, 461b  
 —, occurrence, II. 182d; III. 103b  
 "Argoferment," I. 461c  
**Argoflavin**, I. 134a  
**Argol** or argal, I. 461d  
**Argon**, I. 461d  
 —, detn., II. 681d  
 "Argonin," I. 465d; IV. 26a  
 "Argulan," I. 465d  
**Argyrescin**, III. 27c  
**Argyria**, III. 27c  
**Argyrodite**, I. 466a  
 "Argyrol," I. 466; IV. 26a  
 "Arheol," I. 466a  
 "Arhoine," I. 466a  
**Arbine**, I. 466b; VI. 188a  
**Aricine**, III. 128a, 151c  
**Aristinic acid**, I. 466b  
 "Aristochin," I. 466b; III. 174b  
 "Aristol," I. 466b  
**Aristolochic acid**, I. 466b  
**Aristolochine**, I. 466b

- "*Aristoquinine*," see "*Aristochin*."
- Armagnac**, II. 33b
- Armstrong's** quinonoid theory of colour, III. 308d
- Arnica** flowers and root, I. 466b
- Arnica montana**, I. 466b
- Arnica**, I. 466c
- Arnisterol**, I. 466c
- Aromadendrene**, aromadendrone, I. 466c
- Arrack**, I. 467d
- "*Arrhenal*," I. 482b; IV. 24c
- Arrhenius** equation, constants of, VI. 229a
- of the collision number, IV. 349b; VI. 227c, 229a
- — — heat of activation, II. 531d
- Arrow** poisons, III. 459b
- Arrowroot**, I. 468a; II. 418c
- "*Arsacetin*," I. 468c, 487a; IV. 24d
- "*Arsamin*," I. 468c, 486d
- "*Arsaminal*," I. 468c
- p-Arsanilic** acid, I. 480c
- , acetyl-, sodium salt, I. 468c, 487a
- Arsanthrene**, I. 491c
- Arsenate**, dibarium, I. 644a
- , lead, I. 178d
- Arsenates**, detn., potentiometric, II. 700a
- , qualitative reactions, I. 478c; II. 573b
- Arsenic**, I. 468c
- Arsenical** antimony, I. 439d
- Arsenic**, alloys, I. 472b
- Arsenical** pyrites, I. 469a
- Arsenicals**, aliphatic, I. 481c
- , aromatic, I. 485a
- , aryl-alkyl-, I. 484a
- , asymmetric, optical resolution, I. 484c
- , detn. of As in, II. 622c, 652a
- Arsenical** root, I. 474c
- Arsenicals**, organic, I. 479d
- , in therapeutics, I. 486b
- , volatile, from mould growths, I. 483c
- Arsenic** as trace element, I. 505a
- , Butter of, I. 179c
- , carbide, II. 281a
- , caustic oil of, I. 479c
- , chloride, I. 479c
- , as chlorine carrier, II. 353b
- , compounds, I. 472d
- , in warfare, III. 10c
- , cyclic derivs., I. 494a
- , detection, I. 470a
- , detn., assay, I. 522b
- , —, electrodeposition method, II. 700b
- , —, gravimetric, II. 599c
- , in arsenicals, II. 652a; VI. 361d
- , carbon compounds, II. 622c, 652a; VI. 361d
- , food, II. 202d
- , —, hydrogenation analysis, VI. 361d
- , —, micro-method, II. 633b
- , —, potentiometric, II. 700a
- , —, volumetric, II. 651d
- , disulphide, I. 479a
- , glass, I. 475c
- , in hops, II. 92c
- , rice, II. 406c
- , native, I. 469a
- Arsenic oxide**, I. 478b
- , pentasulphide, I. 479c
- , pentoxide, I. 478b
- , qualitative reactions, II. 551d, 573b
- , —, rare metals present, II. 551d, 550d
- , removal from hydrochloric acid, III. 76b
- , sulphides, I. 479a
- , trichloride, production, I. 479c; III. 10d
- , trihydride, I. 472d
- , triiodide, I. 479d
- , trioxide, I. 473a
- , trisulphide, I. 479b
- , white, vitreous, I. 475c
- Arsenillo**, I. 533c
- Arsenious** anhydride, I. 473a
- , oxide for glassmaking, V. 558c, 560a
- Arsenites**, qualitative reactions (see also Arsenic), II. 573b
- Arseniuretted** hydrogen, I. 472d
- Arsenobenzene**, 3:3'-diamino-4:4'-dihydroxy-, I. 491b
- Arsenobenzenes**, I. 491a
- "*Arsenobillon*," I. 491b
- Arsenoklasite**, I. 496c
- Arsenolite**, I. 469a, 476a
- Arsenopyrite**, see Mispickel.
- Arseno-stibinobenzenes**, I. 492d
- Arsine**, I. 472d
- , chlorovinylchloro-, III. 11a
- , detection (see also Arsenic, detection), II. 573b, 682a
- , detn., gravimetric, II. 682a
- Arsinic** acid, dimethyl-, II. 188b
- Artabotrine**, I. 496d
- Artemisia** spp., I. 4c, 5a, 6a; V. 263c
- Artemisin**, I. 497a
- "*Arterenol*," I. 117d, 497a
- Artichoke**, I. 497a
- , Chinese, I. 497a
- , globe, I. 197a
- , Japanese, I. 497a
- , Jerusalem, I. 497a
- Artificial** silk, see Acetate silk
- , dyes; Cellulose; Dyeing; Dyes, azo; Fibres, artificial, or rayon.
- , transmutation, I. 542b
- Artisil** dyes, I. 42a
- Artocarpus integrifolia**, A. spp., I. 497d; II. 85d
- Arum maculatum**, I. 497d
- Aryane**, III. 28b
- Arylacetylenes**, I. 117d
- Arylacridines**, I. 127c
- Aryladipic** acids, I. 144b
- Arylamines**, reaction with carbon monoxide, II. 350d
- Arylguanidines**, VI. 144d, 147a
- Arylstibonic** acids, I. 436a
- Asafetida**, I. 497d
- "*Asaprol*," I. 4c; IV. 30a
- Asaraldehyde**, I. 498d
- "*Asarcoloy*," II. 192d
- Asarone**, I. 498d; II. 401b
- Asaronic** acid, I. 498d
- Asarum arifolium**, A. canadense, I. 498d; IV. 397d, 400a
- , spp., eugenyl methyl ether from, IV. 394d
- Asbarg**, I. 499a
- "**Asbestic**," I. 500d
- Asbestine**, I. 499b
- Asbestos**, I. 499c
- "**Asbestos**, blue," I. 499d; III. 429d
- Asbestos** in plastics, II. 415b, 479b
- , serpentine, I. 499c
- , varieties, I. 499d
- Asbolan**, asbolite, III. 214b
- Ascaridole**, I. 501a; III. 24d
- "**Ascarite**," II. 882b
- Ascharite**, II. 35b
- Asclepias** cotton, A. spp., I. 501c
- l-Ascorbic** acid (see also Vitamin C), I. 501c; IV. 311b
- Ascosterol**, IV. 325c
- Asduana**, II. 105b
- "**Aseptol**," I. 503c
- Ash**, I. 503c
- Ashbury** metal, I. 445d
- "*Asiphil*," see Asyphil.
- Asmanit**, I. 511c
- Asparaginase**, I. 511c
- Asparagine**, I. 511d, 514d; II. 141b
- Asparagus**, I. 514c
- , stone, I. 440d
- Aspartase** (in B. coli), I. 514d
- Aspartic** acid, I. 514d
- Aspergillus**, asparaginase in, I. 511c
- , niger (see also Fermentation, mould), II. 84b; IV. 282d
- , oryzae, IV. 315d
- , spp. in fermentations, see Fermentation, mould.
- Asperula** essence, III. 412d
- Asperula** spp., I. 516a; V. 415c
- Asperulin**, I. 516c
- Asperuloside**, V. 416d
- Asphalt** and bitumen, I. 516d
- Asphodel**, *Asphodelus* spp., I. 517d
- Aspidin**, aspidinol, V. 181b, 182a
- Aspidium filix mas**, A. spinulosum, V. 180d, 182a
- Aspirators**, I. 012a; VI. 359d
- "**Aspirin**," I. 119d, 517d
- "**Aspirin** soluble," I. 517d
- "**Aspirin**," trade names, I. 517d
- Aspirophen**, I. 518a
- "**Asposal**," I. 517d
- "**Asprodone**," I. 518a
- Assaying** (see also Analysis, chemical; individual metals), I. 518a
- Assay** sampling, I. 518b
- , ton, III. 1a
- Assistants**, chemical, in dyeing, IV. 120d
- Astacin**, I. 532a
- Aster chinensis**, I. 532d; II. 234b
- Asteric** acid, I. 532b
- Asterin**, I. 532d; II. 234b; III. 115d
- Astrakanite**, II. 19b
- Astraline**, I. 533a
- Astralit**, I. 533a
- Astralite**, I. 533a
- Astraphloxine**, III. 519c
- "**Astrolit**," I. 533a
- Astrophyllite**, I. 450b
- "**Asyphil**," I. 533b, 547c

- Atacamite**, I. 533c; III. 341c, 350b  
**"Atebrin,"** I. 134a; III. 137b  
**Atelestite**, I. 533c  
**Atisine**, I. 123d  
**Atis root**, I. 533c  
**Atlantone**, I. 533c  
**Atmosphere**, I. 534a  
**"Atocin,"** I. 539c  
**Atomic data** for the elements, I. 539b  
 — number, *see* Atomic data;  
 Atomic structure.  
 — structure, I. 541a  
**"Atonin,"** I. 517d  
**"Atophan,"** (*see also* Cincho-  
 phon), I. 539c, 547a  
**"Atoquinol,"** I. 547a  
**"Atoxyl,"** I. 408c, 480b, 480d,  
 547a  
 —, acetyl-, I. 408c, 187a  
**Attractyl acid**, VI. 86a  
**Attractylis gummifera**, VI. 86a  
**Attractylol**, IV. 393a  
**Atranorin**, I. 547a  
**Atrolactic acid**, I. 547a  
**Atropa belladonna**, I. 603b  
**Atropamine**, I. 547b  
**Atropine**, VI. 203d  
**Atropulol** from *Euonymus*,  
 IV. 400c  
**Atroscine**, *see* Hyoscine.  
**Attacus atlas**, *A. spp.*, I. 171d,  
 V. 80a  
**Attalea cohune**, *A. fumifera*,  
 III. 257d; V. 168a  
**Attar of roses**, I. 547b  
**"Atrosyl,"** I. 547c  
**Aubepine**, I. 376d  
**Aucuba japonica**, I. 517c  
**Aucubigenin**, I. 547c  
**Aucubin**, I. 547c  
**Augelite**, I. 547d  
**Augite**, I. 652a; II. 137c; III.  
 573a; VI. 120a  
 —, syenite building stone, II.  
 137c  
**Auld and Pickle extractor**, IV.  
 580d  
**Auracin G**, I. 131d  
**Auramine** I, II, III, G and O,  
 I. 547d, 518a, 549c  
 —, antiseptic, I. 548d  
 —, N-phenyl, I. 540b  
**Auramines**, N-alkyl, I. 540b  
**Aurantia** or Hexyl, I. 549c;  
 IV. 14d, 480a  
**Aurantia**, V. 50d  
**Aurate**, barium, VI. 116b  
 —, potassium, VI. 116a  
 —, — disulphato-, VI. 117a  
**Aureolin**, III. 219b  
**Auric acid**, VI. 116a  
 —, hydronitrato-, VI. 117b  
 —, chloride, diammino-, VI.  
 116d  
 —, dipyridinodichloro-, VI.  
 113b  
**"Auric chloride, phenyl-,"** VI.  
 121d  
**Auric compounds**, *see also*  
*under* Gold compounds.  
 — oxide, sesquiammino-, VI.  
 116c  
 — sulphide, VI. 116b  
**Auriferous** (telluride, VI. 102a  
**Aurine**, I. 549d  
 —, hexahydroxy-, IV. 401c  
 —, 3:5:3':5':3''-5''- hexameth-  
 oxy-, IV. 401a  
**Auripigmentum**, I. 479b  
**Auriosulphide**, sodium (*see also*  
*under* Gold compounds), VI.  
 116c  
**"Aurobin,"** I. 549d  
**"Aurocantan,"** I. 549d  
**"Aurochin,"** I. 549d  
**Aurocyanides** in gold extrac-  
 tion, III. 480a; VI. 104b,  
 115a  
**Aurofusarin**, V. 56  
**Auroglauzin**, V. 54c  
**Aurophosphin G**, 4G, I. 132d  
**Aurosmirid**, I. 549d  
**Aurosoauric** halides, doubts  
 concerning, VI. 115a, 116b  
**Aurosoauric oxide**, VI. 116b  
**Aurothiosulphate**, sodium,  
 VI. 117d  
 —, —, structure, VI. 118a  
**Aurous** acetylhydride, II. 280b;  
 VI. 118b  
 — acid, hydrobromo-, VI. 113d  
 — bromide, VI. 113c  
 —, —, diammino-, VI. 113d  
 — chloride, and derivs., VI.  
 113d  
 —, —, bisdiethylene thio car-  
 bamido-, VI. 114b  
 — carbonyl, VI. 121d  
 —, dimethyldithioethylene-,  
 VI. 114b  
 — compounds, *see also under*  
*Gold compounds*.  
 — iodide, VI. 114d  
 — oxide, non-existent, VI. 115d  
**Aurum**, VI. 101c  
 — mosaicum or musivum, I.  
 549d  
**Auryl compounds**, *see also*  
*under* Gold compounds.  
 — hydrosulphate, VI. 117a  
 — hydroxide, VI. 116a  
**Aussig** electrolytic cell, III.  
 52b, 67d  
**Austenite**, I. 550a  
**Austinite**, I. 550a  
**Austracamphene** (*d*-cam-  
 phene), I. 237c, 550a  
**Australian wattle**, I. 11c  
**Australite**, I. 533a  
**Autan**, I. 550a  
**Autoclaves**, I. 550b  
**Autolysis**, I. 556c  
**"Autoxidation"** reactions in  
 hydrogen peroxide, VI.  
 340c  
**Autunite** or Calco-uranite, I.  
 558a; II. 393a  
**Auximones**, V. 63b, 74d  
**Auxin**, I. 558b  
**Auxochromes**, III. 308b  
**Avanturine** or Aventurine, I.  
 559c  
**Avena sativa**, VI. 80b  
 — unit, I. 558b  
**Avensin**, VI. 86b  
**Aventurine glass or glaze**, I.  
 559d; VI. 12a  
 — quartz, I. 559d  
**Averrhoa carambola**, II. 275d  
**"Avertin,"** I. 308b, 559d  
**Avignon berries**, I. 560a; VI.  
 498a  
 — grains, I. 559d  
**"Avional,"** I. 253a, 277a  
**Avocado oil**, I. 560a  
 — pear, I. 560b  
**Avogadrite**, I. 560c; V. 60b  
**Avogadro's law**, VI. 412c  
**Awobana**, I. 560c  
**Awobanin**, III. 554c  
**Axin**, I. 560d  
**Axinite**, I. 204d, 560d  
**Axite**, IV. 518a  
**Ayahasco**, II. 182a  
**Azabenzanthrone**, I. 428b  
**Azacyanines**, III. 530a  
**Azadirachta indica**, I. 561a  
**Azafran** or azafranillo, I. 501a  
**Azafrin**, I. 561a; II. 401b  
**Azafrinal-I** and -II methyl  
 esters, II. 395d  
**Azafrin**, relation to carotene,  
 II. 395d  
**Azanthraquinone**, I. 428c  
**Azelaic acid**, I. 561c  
**Azelaone**, I. 562a  
**Azeotropes** (*see also* Distilla-  
 tion, laboratory), I. 178c  
 —, definition, IV. 51b  
 — in analysis, II. 711a  
 —, varieties of, IV. 51b  
**Azeotropic mixtures** with alco-  
 hols, I. 100b  
**Azides**, cyanuric and metallic,  
 I. 562a  
 —, derivs. and detn., I. 580b  
 —, velocity of decomposition,  
 VI. 223a  
**Azidine** dyes, *see* Diamine  
 dyes.  
**Aziminobenzenes**, I. 315d  
**Azimin-compounds**, I. 503d;  
 III. 580c, 593b  
 — naphthalenes, 1:2-, 1:8-, and  
 2:3-, III. 593b  
**Azine** dyes, I. 568a, 578b  
**Azines**, I. 563d; II. 315d; VI.  
 299b  
 —, quinonoid formulae, I. 571a  
**Azo-acid-wool** dyes, tables,  
 IV. 208-210  
 — — — —, constitution, IV.  
 203b  
**Azobenzene**, I. 579c  
**Azocarmine B**, I. 573d  
**Azo-compounds**, detn., II.  
 627b, 707a  
 —, prepn., IV. 193a  
**Azodicarbamidine**, VI. 149c  
**Azo-dyes**, IV. 190a  
 —, —, treatment with form-  
 aldehyde, IV. 226b  
 —, —, —, metallic salts, II.  
 141c, 209c, 224a, 226a  
 —, —, —, and components, identi-  
 fication, IV. 147b, 173a,  
 195a, 239a  
 —, —, applications, IV. 126d,  
 190c  
 —, —, chrome - printing, IV.  
 226d  
 —, —, components and uses,  
 — tables, IV. 200-236  
 —, —, coupling by special  
 methods, IV. 238b  
 —, —, developed on the fibre,  
 IV. 225b  
 —, —, diazotising and coupling  
 reactions, IV. 195a  
 —, —, direct cotton, IV. 215c  
 —, —, —, affinity of, IV.  
 224c  
 —, —, —, from  $\gamma$ -acid, IV.  
 223b  
 —, —, for acetate rayon, IV.  
 234b  
 —, —, —, cotton printing, IV.  
 179a, 226d



- Azo-dyes** for leather, IV. 215a  
 ——— silk, IV. 214d  
 ——— viscoserayon, IV. 231a  
 ——— wool, IV. 203a  
 ———, J-acid coupling component, IV. 222c  
 ———, manufacture and plant, IV. 230d, 238c  
 ———, metal complexes in, IV. 141d, 211c, 214c, 224a  
 ———, mordant, IV. 210a  
 ———, properties, IV. 193d  
 ———, various uses, IV. 230b  
**Azoic bases**, constitution, IV. 232a  
 — coupling components, IV. 228, 229  
 — dyes, IV. 120d, 227b  
 ———, nitrosanunes for printing, IV. 233a  
 — printing mixtures, IV. 231d  
**Azoimide**, I. 580a  
**Azoimides**, aromatic, III. 586c  
 —, preparation from diazonium salts, III. 586c  
**Azo-lake dyes**, IV. 234c  
**Azomethane**, III. 600a  
**Azo-mordant-wool dyes**, mono-, IV. 212a  
**Azonium bases**, I. 564a  
 "Azophenylene," I. 505a  
 "Azophor" stable diazo-compounds, IV. 231c  
**Azo-pigment dyes**, IV. 231c  
**Azorubin**, II. 390a  
**Azote**, I. 582c  
**Azotobacter** and trace elements, I. 507d, 510c  
**Azotoluene**, *o*-amino-, I. 556a  
**Azotometer**, I. 582c; II. 618a, 631b  
**Azoxybenzene**, I. 582c  
**Azulene**, I. 5d, 119d, 583a  
**Azurin**, I. 583c  
**Azurite**, I. 583d; II. 25c; III. 26c, 341c, 355d  
  
**B-Acid**, I. 583b  
**Babassu fat**, in chocolate, III. 88b  
 — oil, III. 213d  
**Babbitt metal**, I. 585a  
**Bablah**, I. 585a  
**Babul gum**, I. 585a  
**Bacilli**, *Bacillus*, see B.  
*B. aceti*, I. 43c; IV. 378a  
*B. anthracis*, V. 395b  
*B. coli*, cytochrome, III. 544c  
*B. curvus*, I. 43c  
*B. kützingianum*, I. 43c  
*B. mesentericus* on bread, II. 84b  
*B. oxydans*, I. 43c  
*B. pasteurianum*, I. 43c  
*B. xylinoideus*, I. 43c  
*B. xylinus*, Brown's, I. 43c, 45b  
**Backman** chambers in bleaching powder production, III. 61b  
**Baco fat**, I. 655a  
**Bacteria**, *Bacterium*, see also B.  
**Bacteria**, chemical action, see Fermentation, bacterial.  
 —, chemiluminescent, III. 23d  
 —, lactic, in butter, II. 160a  
**Bactericides**, see Antiseptics;  
 Disinfectants; Food preservatives.  
*Bacterium tumefaciens*, V. 420d  
**Baddleyite**, I. 585b; II. 67c  
**Badische acid**, I. 1a, 585d  
**Badouin test**, for sesamé oil, II. 167b  
**Bael fruit**, I. 585d  
**Baeumlerite**, I. 585d  
**Bagasse**, I. 585d; II. 497c  
**Baicalin**, I. 585d; VI. 80b  
**Bajri**, II. 482d  
**Bakankosine**, I. 580a  
 "Bakelite" (see also Formaldehyde-phenol resin), I. 586a; II. 308c  
**Bakerite**, I. 586a  
**Bakhar**, I. 586a  
**Baking powders**, I. 586b  
**Balam fat**, II. 32b  
**Balance**, I. 587a  
**Balata**, IV. 157a  
**Balbiano's acid**, II. 218a  
**Balbul bark**, I. 11c  
**Baldwin's phosphorus**, II. 222c  
**Baljet reaction** of carbac glycosides, II. 383d  
**Ballas**, III. 547d  
**Ball-diorite**, IV. 8b  
**Ballistic pendulum**, IV. 548c  
**Ballistite**, I. 614c; IV. 518b  
**Balm of Gilead**, I. 614d  
**Balsam** (see also Balm), I. 614d  
 —, copaiba, III. 337b  
 —, Gurjun, and its oil, III. 337c; VI. 156c  
 —, Illurin, III. 338b  
 —, Mecca, I. 614d  
**Balsamo blanco**, I. 616d  
**Balsamodendron sup.** gum resin, I. 658c  
**Balsam**, Peru, and B. Tolu, I. 610b, 617c; III. 180a  
**Balsams**, I. 614d  
 —, xanthorrhoea, I. 618b  
**Baltimore oil**, III. 21c  
**Bambara-** or bamboo-fat, I. 651b  
**Bamboo**, I. 618d  
**Bambuk-butter**, I. 651b  
**Banana**, I. 618d  
 — fibre, I. 1a, 618d  
**Bandrowski's base**, VI. 171d  
**Banisteria caapi**, II. 182a; VI. 180a  
**Banisterine - harmine**, II. 182a; VI. 186b  
**Bacbab tree**, *Adansonia digitata*, I. 141b  
**Baphiin**, baphnitin, baphnitone, I. 650b, c  
**Baptigenin**,  $\psi$ -baptigenin, I. 619c; V. 259d; VI. 80b  
**Baptin**, I. 619c  
**Baptisia tinctoria**, I. 619a; VI. 80b  
**Baptisin**,  $\psi$ -baptisin, I. 619c; V. 259d; VI. 80b  
**Baptitoxine**, III. 542c  
 "Baratol," I. 619c; IV. 464b  
**Barbaloin**, isobarbaloin, I. 202a, c  
**Barbatic acid**, I. 619d  
**Barbatolic acid**, I. 619d  
**Barberry**, I. 619d  
 "Barbital," I. 623a  
**Barbituric acid**, I. 620c  
 —, acyl derivs., I. 624a  
 —, 1-dihromopropyl-5:5-diethyl-, IV. 7c  
 —, 1:5-dimethyl-5-cyclohexenyl-, IV. 415b  
**Barbituric acid**, di- and trimino-, I. 620c  
 — from urea, II. 352d  
 —, halogen derivs., I. 621c  
 —, hydroxy-, I. 625a  
 —, N-substituted derivs., I. 621a  
 —, 5-nitro-, I. 627a  
 —, polysubstituted derivs., I. 622a  
 —, salts, I. 620d  
 acids, alkyl and aryl, I. 621a  
 —, amino-derivs., I. 628c  
 —, condensation with aldehydes and ketones, I. 629d  
 —, diazo compounds, I. 630b  
 —, C-substituted derivs., I. 621a  
 —, detection and detn., I. 623b  
 —, 5:5-disubstituted, I. 621d  
 —, ether like derivs., I. 623d  
 —, isonitroso-, I. 620c  
 —, substituted, pharmacological properties, I. 623a  
 —, trade names, I. 623a  
 —, (thio-, I. 622c  
**isoBarbituric acid**, I. 630d  
**Barilla** or bariller, I. 630d; II. 448c  
**Barite**, I. 651a  
**Barium**, I. 631a  
 — alloys, I. 632a  
 — aluminates, I. 284c, 641d  
 — amalgam, I. 632a  
 — amide, I. 638d  
 — ammonium, I. 638d  
 — arsenates, I. 641a  
 — as trace element, I. 505a  
 — azide, I. 563a, 580d, 639a  
 — bromide, I. 630d  
 — carbide, I. 637d  
 — carbonate (see also Witherrite), I. 638a  
 — for glassmaking, V. 561b  
 — in brick-making, II. 126a  
 — carbonyl, II. 357c  
 — chlorate, I. 636c  
 — chloride, I. 635a  
 — chlorite, I. 636b  
 — chromate, I. 642c; III. 111d  
 — cyanide, III. 491d  
 — defn., gravimetric, II. 589b  
 —, volumetric, II. 653b, 700a  
 — dichromate, I. 642c; III. 111d  
 — dimetaphosphate, I. 643b  
 — dithionate, I. 642a  
 —, drop reaction, II. 570d  
 — ferrocyanide, III. 470b  
 — fluoride, I. 637c  
 — hexametaphosphate, I. 643b  
 — hydrosulphide, I. 640d  
 — hydroxide, I. 634a  
 — in Brazil nuts, II. 67c  
 — iodate, I. 637b  
 — iodide, I. 637a  
 — ions, action on prothrombin, II. 23c  
 — manganate, I. 642d  
 — manganite, I. 643a  
 — monometaphosphate, I. 643b  
 — monosulphide, I. 640a  
 — nitrate, I. 636b  
 — explosives, IV. 404b  
 — nitrite, I. 639b  
 — orthophosphates, I. 643b  
 — ortho-thioarsenate, I. 644b

- Barium** oxide, I. 632*b*  
 — oxybromides, I. 636*d*  
 — oxychloride, I. 636*b*  
 — oxyiodide, I. 637*b*  
 — -parisite, III. 364*a*  
 — pentasulphide, I. 641*a*  
 — perchlorate, I. 636*c*  
 — periodate, I. 637*b*  
 — permanganate, I. 642*d*  
 — pernitride, II. 222*a*  
 — peroxide, I. 633*a*  
 — — hydrate, I. 635*a*  
 — phosphide, I. 643*a*  
 — platinocyanide, III. 487*d*  
 — potassium ferrocyanide, III. 470*c*  
 — pyrophosphate, I. 644*a*  
 — pyrosulphate, I. 642*a*  
 — qualitative reactions, II. 553*c*, 567*b*  
 — —, rare metals present, II. 555*d*, 556*d*  
 — selenate, I. 642*b*  
 — selenide, II. 642*b*  
 — selenite, I. 642*b*  
 — silicates, I. 644*c*  
 — silicides, I. 644*b*  
 — sodium sulphate, I. 612*a*  
 — subchloride, I. 635*a*  
 — suboxide, I. 632*b*  
 — sulphate (*see also* Baryte), I. 641*b*  
 — —, acid, I. 641*c*  
 — — for glassmaking, V. 501*b*  
 — — in paints, II. 3*a*  
 — —, mineral, I. 651*a*; II. 20*d*  
 — —, phosphorescent, II. 26*d*  
 — sulphate, I. 641*b*  
 — sulphhydrate, I. 640*c*, *d*  
 — tetrasulphide, I. 641*a*  
 — tetroxide, I. 634*a*  
 — thiocarbonate, I. 641*b*  
 — thiosulphate, I. 642*b*  
 — titanate, I. 645*a*  
 — trimetaphosphate, II. 643*b*  
 — trisulphide, I. 641*a*  
**Barker** electrolytic cell, III. 67*d*  
**"Barkite,"** I. 645*a*  
**Barley**, I. 645*b*; IV. 596*d*  
 —, pearl, I. 645*b*  
**Barrn**, II. 78*d*  
**Barrels**, glue-lined, for turpentine, I. 250*a*  
**Barreswil's** solution, I. 648*d*  
**Barwood**, I. 650*b*; II. 200*c*; IV. 120*c*  
**Barylite**, I. 650*d*, 685*b*  
**Baryta**, I. 631*a*, 632*b*  
 — in respirators, III. 20*c*  
**Baryte** or barytes, I. 631*b*, 641*b*, 651*a*  
**Barytes** in plastics, II. 476*b*  
**Barytocalcite**, I. 631*d*  
**Baryto-celestite**, I. 631*b*  
**Basalt**, I. 651*d*  
**Basanite**, I. 652*a*  
**Basanti**, II. 430*d*  
**Base**, definition, VI. 248*a*, 249*a*  
 — exchange reactions, VI. 218*b*, 219*a*  
**Bases**, strength, VI. 248*d*  
**Basil**, essential oil, I. 652*c*  
**Basile** electrolytic cell, III. 54*b*  
**"Basogrelit,"** III. 63*d*  
**Bassia** fats, I. 652*d*  
 — Mahwa or Mowrah flowers, I. 655*b*  
**Bassia** spp., I. 653*a*, 655*b*; II. 169*d*  
**Bassia** tallow, I. 653*a*  
**Bassisterol**, I. 653*d*  
**Bastorin**, VI. 156*b*  
**Basswood** oil, I. 655*c*  
**Bast**, II. 461*b*  
**Bastnäsite**, I. 655*d*  
**Batatas**, *B. edulis*, I. 655*d*  
**Bat-guano**, V. 61*a*  
**Bath brick**, I. 656*c*  
 — stone, V. 329*a*  
**Bauxite**, I. 264*c*, 656*c*  
 — for alumina production, I. 265*d*  
 —, refining agent for oil, I. 657*b*  
**Bavenite**, I. 658*a*  
**Bay**, essential oil, I. 658*b*  
**Bayer acid**, I. 658*c*  
**Bayerite**, I. 284*b*  
**Bellium**, I. 658*c*  
**Beam dyeing**, IV. 130*c*  
**Bean**, I. 658*d*  
 — oil (*see also* Soya bean oil), I. 660*a*  
 —, ordeal, II. 198*d*  
**Beans**, adsuki or adzuki, I. 155*b*, 658*d*  
 — broad, I. 658*d*  
 — French, I. 659*a*  
 — gram, I. 659*a*  
 — jack, I. 659*a*  
 — kidney, I. 659*a*  
 — Lima, I. 659*a*  
 — locust, I. 658*d*  
 — Mung, I. 659*c*  
 — "Shell," I. 659*a*  
 — "Snap," I. 659*a*  
 — soja, soy, soya, I. 659*c*  
 — velvet, I. 659*c*  
**Bearberry** leaves, I. 660*b*  
**Bearing metal**, I. 446*a*  
**Bebeerine**, *d*-, *l*- and *r*-, I. 660*c*; II. 182*a*  
 — *l*-Bebeerine in curare, III. 459*d*  
**Bébé** oil, VI. 510*b*  
**Beckelite**, I. 661*a*  
**Beckerite**, I. 302*c*  
**Beckmann's** freezing-point method, III. 442*a*  
**Becquerelite**, I. 661*b*  
**Bedeguar**, V. 420*c*  
**Beech-nut** oil, I. 661*c*  
**Beech tar**, I. 661*b*  
**Beer** analysis, Plato factor I. 104*a*  
**Beeswax** in candles, II. 263*b*  
 — chocolate, tests for, II. 187*a*  
**Beet**, I. 661*c*  
**"Beetle"** plastics, I. 662*b*  
**Beetling** textiles, II. 461*c*; V. 188*d*  
**Beet** slices as feeding stuff, IV. 596*c*  
 — "tops," IV. 596*d*  
**Begass**, I. 585*d*  
**Behenic acid**, I. 662*d*  
 — — in rice, II. 494*b*  
**Behenic acid**, oxidation, II. 67*b*  
**Beidellite**, I. 663*a*, III. 196*a*  
**Belite**, II. 111*b*  
**Belladonna**, belladonnine, I. 663*b*  
 —, physiological effect, II. 198*d*  
**"Bellite,"** I. 663*b*; IV. 405*c*  
**Bell jar** (Aussig) cell, III. 52*b*  
 — metal, I. 663*b*  
**Beluga** leaf, II. 102*a*  
**Bengal kino**, II. 157*d*  
 — lights, I. 663*b*  
**Benitoite**, I. 663*c*  
**Ben** oil, I. 663*c*  
**Bentonite**, I. 663*d*; III. 106*a*; IV. 247*a*  
**"Benzacetin,"** I. 664*a*  
**Benzaconine**, I. 121*d*  
**Benzal chloride**, I. 664*a*  
**Benzaldehyde**, I. 664*a*  
 —, compounds with sugars, II. 290*a*  
 — ethylacetal, I. 37*b*  
 — from benzal chloride, I. 194*b*, 664*b*  
 — toluene, II. 428*a*  
 — in cherry-laurel oil, III. 26*a*  
 — sugar separations, II. 293*c*  
 —, *p*-nitro-, II. 293*c*  
 —, substitution derivs., I. 655*d*  
**Benzal diacetate**, I. 38*d*  
**Benzalmalonic acid**, I. 196*a*  
**Benzamine**, IV. 399*b*  
 — hydrochloride, I. 667*a*  
**Benzanthraccene**, carcinogenic action, II. 378*d*  
**Benzanthrone**, I. 206*a*, 388*b*, 409*d*  
**Benzanthronequinoline**, I. 413*d*  
***m*-Benzdioxynanthraquinone**, I. 212*d*, 222*a*  
**"Benzedrine,"** IV. 318*a*  
**Benzene** and homologues, I. 667*a*  
 —, detection, I. 675*a*  
 — 2-azo-4-nitrophenol, *p*-bromo-, III. 597*a*  
 — azo-phenyl-2-naphthylamine, I. 508*b*  
 — *p*-bisdiazonium chloride, III. 581*d*  
 — bromo-, carcinogenic compounds from, II. 378*c*  
 — carbon disulphide in, II. 338*b*  
 — chloro-derivs., I. 677*c*  
 —, in fumigants, II. 344*a*  
 —, — phenol prepn., II. 305*b*  
 —, — warfare, III. 10*c*  
 —, — prepn., III. 11*a*  
 —, detection in air, I. 675*b*; II. 682*a*  
 —, detn., colorimetric, I. 675*b*; II. 677*d*  
 —, — in air, II. 677*d*, 682*a*  
**Benzenediazoaminoazobenzene**, III. 590*a*  
**Benzenediazonium**, III. 590*c*  
 — *o*-carboxylate, III. 593*a*  
 — chloride, III. 581*b*  
 — hydroxide, III. 590*c*  
 — nitrate, III. 581*b*  
 — sulphate, III. 581*b*  
 — *p*-sulphonate, III. 592*d*  
**Benzenediazo-oxide**, potassium, labile and stable, III. 597*c*  
**Benzenediazosulphonates**, *syn*- and *anti*-, III. 598*d*  
**Benzene**, *o*-dibromo-, conversion into catechol, II. 430*c*  
 — dicarboxylic acids, phosphors, II. 224*b*  
 —, *o*-dichloro-, catechol from, II. 430*b*  
 —, *o*-dihydroxy-, II. 429*c*  
 —, dinitro-derivs., I. 677*a*  
 —, —, for explosives, IV. 465*b*

- Benzene** from phenol, II. 306d  
 —, hexa-amino-, I. 316d  
 —, hexachloro-, II. 321b  
 —, hexahydroxy-, VI. 225b  
 —, hydrocarbons from acetylenes, I. 86c  
 — in petroleum, I. 466d  
 —, nitro-, for explosives, IV. 465b  
 —, —, in fumigants, II. 344a  
 —, —, prepn., I. 675c  
 —, oxidation, II. 428a  
 —, penta-amino-, I. 310c  
**Benzenes**, tetra-amino-, I. 310c  
 —, triamino-, I. 310c  
**Benzene** sulphonhydrazide, luminescence, III. 23d  
 — toluene mixtures, separation by distillation, IV. 41d, 49a  
 —, trinitro-derivs., I. 677c  
 —, —, explosive, IV. 465d  
 —, trinitrotriazido-, IV. 543a  
 —, vapour, detection and detn., I. 675b; II. 682a  
 —, water mixtures, distillation, IV. 37a  
**Benzhydrazide**, VI. 300a  
 —, *o*- and *p*-chloro-, I. 197b  
 —, luminescence, III. 23d  
 —, *p*-nitro-, and *m*-nitro-, I. 197a, b  
**"Benzidam,"** I. 372c  
**Benzidine**, I. 678d; IV. 11c  
 —, 3,3'-dichloro-, IV. 12c  
 —, 3,3'-dimethoxy-, IV. 12d  
 —, 2,2'-disulphonic acid, IV. 12c  
 —, 3,3'-disulphonic acid, IV. 12c  
 —, 3-ethoxy-, IV. 12d  
 —, 3-nitro-, IV. 12c  
 —, rearrangement, IV. 11c  
 —, sulphone disulphonic acid, IV. 12d  
 —, 3-sulphonic acid, IV. 12c  
**Benzil**, J. 678d  
**Benzilic acid**, II. 363b  
 —, —, change, II. 363b  
**Benzimidazoles**, I. 315c  
**Benzine** bone grease, VI. 23d  
**"Benzinoform,"** I. 678d  
**Benzoates**, qualitative reactions, II. 570b  
**"Benzocaine,"** I. 366b, 678d  
**Benzoflavine**, I. 132b  
**Benzoglyoxalines**, I. 315c  
**Benzoic acid**, I. 678d  
 —, *p*-amino-,  $\beta$ -diethyl-aminomethyl ester, hydrochloride, I. 1c  
 —, —, ethyl ester, I. 366b  
 —, derivs. in food, detection, V. 301b  
 —, esters, I. 680c  
 —, *p*-hydroxy-, oxidation, II. 439a  
 —, —, in butter, II. 108a  
 —, —, food, detection and detn., V. 300d  
 —, *o*-iodoxy-, ammonium salt, I. 305a  
 —, —, production, II. 428a  
 —, —, qualitative reactions, II. 570b  
 —, salts, I. 680c  
 —, acids, hydroxy-, from phenol, II. 307a  
 —, acid, substitution derivs., I. 680d  
**Benzoic acid**, 3,4:5-trihydroxy-, V. 417a  
 —, anhydride, I. 681c  
**Benzoic acid**, I. 140d, 196b, 682b  
 —, oleum, I. 667a  
 —, Palembang, Penang, Siam, and Sumatra, I. 615a  
**Benzoic acid** as motor fuel, I. 671a  
**Benzoic acid** or benzoic (see also Benzene), I. 667a  
 —, recovery by active charcoal, III. 270d  
 —, refining by silica gel, III. 267d  
**Benzoic acid** from coke-oven gas, III. 266a  
**Benzoic acid** specification, II. 472b  
**Benzonaphthol**, I. 682b  
**Benzophenone**, I. 682c  
 —, 2,3:4-trihydroxy-, I. 207a  
**Benzo- $\gamma$ -pyrone**, III. 115c  
**Benzoquinone**, pigments from, II. 280b  
**"Benzosalin,"** I. 682c  
**"Benzosol,"** I. 682c; VI. 140c  
**Benztiazoles**, I. 315d  
**Benzttrichloride**, I. 682c  
**Benzo- $\gamma$ -pyrone**, I. 682a  
 —, peroxide, II. 373a  
 —, in flour, II. 81a  
**Benzyrene**, carcinogenic activity, II. 379a  
**Benzyl acetate**, I. 682c  
**Benzylamine** in vulcanisation, II. 343c  
**Benzylaniline**, I. 308b  
**Benzyl benzoate**, I. 682c  
 —, —, in lacquers, II. 479a  
 —, bromide, prepn., III. 10d  
 —, butyl phthalate in lacquers, II. 472c  
 —, cellulose in plastics, II. 477d  
 —, lacquers, II. 478c  
 —, chloride, prepn., III. 10d  
 —, cyanide, bromo-, in warfare, III. 9a, 10d  
**Benzylidene-oxide**, potassium, III. 600b  
**Benzyl esters**, I. 682c  
**Benzylisoeugenol**, IV. 399d  
**Benzylguaiacol**, VI. 141c  
**Benzylideneacetone**, I. 190a, 682c  
**Benzylideneacetophenone**, II. 518c  
**Benzylideneaniline**, I. 308b  
**Benzylidene chloride**, I. 664a  
**Benzyl iodide**, prepn., III. 10d  
**Benzylphenylhydrazine**, VI. 301c  
**Benzylphenylhydrazones** of sugars, II. 293a  
**Berbamine**, VI. 406c  
**Berberine**, I. 619d, 682d  
**Berberis vulgaris**, *B. spp.*, I. 619d, 620d, 682d  
**Berberry**, I. 619d  
**Bergamot**, essential oil, I. 683d  
**Bergapten**, I. 684a, b; V. 171a  
**Bergblau**, II. 25c  
**Berger process** (Aluminium), I. 268c  
**Bergmann and Junk test**, IV. 515c  
**Bergmehl**, III. 579a  
**Beri-beri**, I. 683b  
**Berli's extractor**, IV. 589c  
**Berthierite**, I. 439d  
**Bertram-Walbaum**, reagent, II. 237c, 255a  
**Bertrandite**, I. 684b  
**Beryl**, I. 264d, 684c; VI. 13c  
 —, artificial, V. 513a  
**Beryllium** acetate, basic and normal, VI. 20b  
 —, acetylde, VI. 10d  
 —, alloys, VI. 15b  
 —, aluminate, III. 119a  
 —, aluminium group, qualitative separation, II. 557c  
 —, and hydrogen, VI. 15c  
 —, arsenate, VI. 19c  
 —, bromide, VI. 17b  
 —, bronze, III. 353b  
 —, carbide, II. 218c; VI. 10d  
 —, carbonate, VI. 20a  
 —, chloride, VI. 10c  
 —, detn., gravimetric, II. 587b  
 —, —, volumetric, II. 653c  
 —, drop reaction, II. 580a  
 —, electrolytic, prepn., VI. 14d  
 —, emission spectrum, VI. 14d  
 —, fluoride, VI. 16a  
 —, hydroxide, VI. 15d  
 —, iodide, and amines, VI. 17b, c  
 —, nitrate, VI. 19a  
 —, nitride, VI. 18d  
 —, organometallic compounds, VI. 20d  
 —, oxide, VI. 15c  
 —, mineral, II. 106c  
 —, perchlorate, VI. 17b  
 —, periodate, VI. 17c  
 —, phosphates, VI. 19b  
 —, phosphide, VI. 19b  
 —, qualitative reactions, II. 555b, 556d, 560d  
 —, selenate, VI. 18d  
 —, selenide, VI. 18c  
 —, selenite, VI. 18c  
 —, sulphate and derivs., VI. 18a  
 —, sulphide, VI. 17c  
 —, sulphite, VI. 17c  
 —, tellurium compounds, VI. 18d  
**Berylliofluorides**, VI. 16b  
**Beryllonite**, I. 685b; VI. 13c  
**Berzelianite**, I. 685c  
**Berzelite**, I. 685c  
**"Betacaine,"** I. 667a; II. 31b  
**Betafite**, I. 685c; II. 19c  
**"Betaform,"** I. 685d  
**Betaine** hydrochloride, I. 120b  
 —, in cabbage, II. 182d  
 —, —, ergot, IV. 331d  
**Betaines**, I. 685d  
**Beta maritima**, I. 601c  
**Betanidin**, I. 687b  
**Betanin**, I. 381d, 687c  
**Beta vulgaris**, I. 601c, 687b  
**Betel leaves**, I. 687c  
 —, nut, I. 458a  
**Betitol**, I. 687c  
**"Betol,"** I. 687c; IV. 29d  
**Betonidine**, I. 688c  
**Bettendorff's test**, I. 471d  
**Betterton process**, II. 204b  
**Betula spp.**, fatty oil, I. 655c  
**Betulin**, I. 687c  
**alloBetulin**, I. 687d  
**Betulol**, I. 687c  
**Betulolic acid**, I. 688a  
**"Bexoid,"** II. 480a  
**Bezetta**, I. 688a  
**Bezoar**, I. 688a  
 —, stones, oriental, IV. 270d  
**Bhang**, I. 688b  
**Bicarbonates**, qualitative reactions, II. 509c

- Bicaruretted hydrogen**, IV. 372b
- Bichroux** glass rolling process, V. 593c
- "Bichromate"** or **"bichrome,"** III. 110c
- Bickford's safety fuse**, IV. 456c
- Bicuculline**, I. 145b
- Bicubhya fat**, I. 088b
- Bieber's reagent**, I. 200c
- Bigitalinum crystallisatum**, II. 384c
- Bignonia chica**, *B. tocoma*, I. 688b; II. 275c
- Biguanide**, VI. 143d
- Bilkaconitine**, I. 123b
- Bilberry**, I. 688c
- Bile**, I. 689a
- acids, I. 689b
- , relation to cholesterol, III. 89b
- mucin, I. 690a
- pigments, I. 690d
- salts, I. 689c
- Bilicyanin**, I. 200c
- Biliposol**, I. 692a
- Bilirubic acid**, I. 691b, *d*
- neoBilirubic acid**, I. 691b, *d*
- Bilirubin**, I. 200c, 689a, 690d, 691a
- Bilival**, I. 692a
- Biliverdin**, I. 689a, 690d
- Billiter-Leykam** electrolytic cell, III. 53a
- Bilobal**, V. 536a
- Bios** (see also Growth-promoting-factor), I. 692a; VI. 138d
- in brewing yeast, II. 98c
- "Bios I"** II. 98c; VI. 495c
- Biotin**, VI. 130a
- Birch-bark oil**, I. 692b
- tar oil, I. 692c
- white, oil, I. 692c
- Bird lime**, I. 692c
- "Birmabright,"** I. 253a, 277c
- "Birmasil,"** I. 253a, 277c
- "Birmidium,"** I. 277a
- Biotation** of glucose, II. 285c
- Bisabolene**,  $\alpha$ -,  $\beta$ - and  $\gamma$ -, I. 693a
- in carrot seed oil, II. 404b
- trihydrochloride, I. 693c; IV. 591c
- Bisabolol**, I. 693b
- Bisacridonyl**, I. 130b
- "Bisciniod,"** I. 693d
- "Biscoclaurine alkaloids,"** II, 481b; III. 230c; VI. 490c
- Biscuit** (ceramics), VI. 2c
- Bisdiazocamino-compounds**, aromatic and mixed aliphatic-aromatic, III. 590d
- Bisdiazonium salts**, III. 581d
- "Bismal,"** I. 700d
- "Bismarsen,"** I. 694a
- Bismite**, I. 694a
- Bismochite**, I. 694a
- "Bismo-cymol,"** I. 694a
- "Bismogenol,"** I. 694a
- "Bismoid,"** I. 694a
- Bismuth**, I. 694b
- alloys with cadmium, lead, and tin, I. 698a
- barley, I. 694d
- carbonate, basic, I. 699d
- chloride, basic, as cosmetic, II. 3a
- chromate, III. 113c
- Bismuth chrysophanate**, I. 701a
- , detn., assay, I. 522c
- , —, colorimetric, II. 670b
- , —, electrodeposition method, II. 700b
- , —, gravimetric, II. 690d
- dibromohydroxynaphthoate, basic, I. 701a
- , drop reaction, II. 580a
- extraction by wet methods, I. 696b
- from argentiferous lead, I. 695d
- flue dust, I. 695c
- gallate, basic, I. 700d; III. 558d
- hydroxyiodogallate, I. 700a
- glance, I. 703a
- hydride, I. 699b; VI. 305a
- hydroxide, I. 694a, 699c
- in anode slimes, I. 695c
- candle wicks, II. 265a
- Bismuthine dihalides**, I. 701c
- Bismuthines**, arylhalogen-, I. 701c
- , trialkyl-, I. 701b
- , triaryl-, I. 701b
- Bismuthinite**, I. 703a
- Bismuth in metals and alloys**, effect of, I. 698d
- iodide, I. 700b
- lactate, I. 700c
- liquation, I. 691d
- $\beta$ -naphtholate, I. 701a
- nitrate, I. 699d
- , compounds with sugars, I. 702d
- ochre, I. 694a
- Bismuthoidol "Robin,"** I. 703b
- Bismuth**, organo-compounds, I. 701
- oxide in catalyst for  $\text{HNO}_3$  production, II. 424c
- oxychloride, I. 700b
- oxyiodogallate, I. 171d
- , pharmaceutical quality, I. 696c
- , phosphorescence in calcium sulphide, II. 230a
- , properties and uses, I. 697b
- , purification of metallic, I. 696c
- pyrogallate, I. 701a
- , qualitative reactions, II. 551b, 573c
- , —, rare metals present, II. 554d, 556d
- salicylate, I. 700c
- smelting, I. 695a
- sodium gluconate, I. 692a
- sulphite, I. 700b
- tribromophenolate, I. 701a
- wire in physics, I. 698a
- Bismuthyl salts** of organic acids, I. 702c
- Bismutite**, I. 703b
- "Bismutose,"** I. 703b
- Bismutotantalite**, I. 703b
- "Bisocol,"** I. 703b
- "Bistovol,"** I. 489c
- Bistrie**, I. 703c
- "Bis-trypaflavin,"** I. 130d
- Bisulphite pulp**, II. 401c
- Bitter apple**, III. 294a
- Bittern**, I. 703c
- Bitter-sweet**, I. 703c
- wood, I. 703c
- Bitumen**, I. 516d
- emulsions, IV. 302b
- Bituminous coatings**, III. 395d
- Bixa orellana**, I. 378a
- Bixa seed**, I. 378a
- Bixin**, I. 378b; II. 401b
- dialdehyde, II. 399b
- , similarity to mycanthin, II. 440a
- Black**, Acetylene, I. 86d, 96c; II. 312d
- , Acid Alizarin, SE, I. 207a
- , Alizarin Cyanine, G, I. 228b, 393a
- , F, SRA, I. 207a
- , P, I. 229b, 397a
- , S, I. 200d
- , Aniline, I. 376c, 579c; II. 509c; IV. 127c
- Blackarm**, V. 139a
- Black ash**, II. 1a
- band iron-stone, II. 519d
- Blackberries**, II. 1a
- Blackboy gum**, I. 618a
- Black**, Brilliant Alizarin, I. 206d
- , Brunswick, II. 39a, 119b
- , Caledon, 218M, NB, I. 424c
- , Direct, AC, I. 424c
- , Carbon, I. 77a; II. 312b
- , specification, II. 473b
- Catechu, I. 11c
- chalk, II. 1b
- , Chbanone, B, I. 423c
- cores, in ceramics, III. 198b
- diamond, II. 356d
- , Dispersol Dmzo, AS, I. 41a
- , eupitone, IV. 401c
- flux, II. 1b
- , Gas, II. 312b
- grease, II. 1c
- haw, II. 1c
- hellebore, II. 1c, 387b; VI. 200a
- , Indanthrene Direct, G, RB and RL, I. 424c
- Blacking**, II. 1d
- Black**, Jomanno, AS, I. 40b
- , Ivory, II. 311d
- jack, II. 2d, 19a
- Lamp, III. 423c
- lead, II. 2d, 309b, d, 313d
- liquor, I. 55a; II. 2d
- , Paradone Direct, I. 424c
- , (H.), I. 424c
- powder, II. 2d
- Blacks**, Acid, IV. 208b, 210b
- , Anthrone, I. 424c
- Blackstrap**, II. 2d
- Black**, Thermatomic, II. 312b
- tin, II. 419c
- Blanc de fard**, I. 700a
- perle, see White, Pearl.
- d'Espagne, I. 700a
- fixe, I. 642a, 651d; II. 3a
- in plastics, II. 476b
- process, I. 208c
- "Blanc rule," II. 374a
- "Blankit"** (sodium dithionite), II. 3a
- Blanquette**, II. 3a
- Blast-furnace gas**, II. 345a; V. 370b
- furnaces, action of carbon monoxide in, II. 351a; V. 370b
- "Blastine,"** IV. 464d
- Blasting gelatine**, II. 3a; IV. 241d
- Bleaching**, II. 3c; V. 183c
- agents, perborates in, II. 52a

**Bleaching** earthen, IV. 248b  
 — of flour, II. 81b  
 — — silk, II. 18b  
 — — powder, II. 6a, 19a; III. 36d, 60a  
**Bleach** liquor, III. 62b  
 "Blenal," II. 19a  
**Blende**, II. 19a  
**Bleu celeste**, II. 25a; III. 219a  
 — d'azur, II. 19a; III. 219c  
 — de saxe, II. 19a; III. 219c  
**Blind** coal, II. 19a  
**Blister** steel, II. 19a  
**Bloedite**, II. 19b  
**Blomstrandine**, II. 19b  
**Blomstrandite**, I. 685c; II. 19c  
**Blood** (see also Hæmin), II. 19c  
 —, action of carbon monoxide on, II. 351b; VI. 166a  
 — anticoagulants, II. 24b  
 — cements, I. 43a  
 — coagulation, II. 22c  
 —, defibrination, II. 24b  
 —, dried, fertiliser, V. 60b  
 — glycolysis and clotting, II. 22d  
 — meal, II. 21d  
**Bloodstone**, II. 25a  
**Blood** sugar in diabetes, VI. 496d  
 —, test for carbon monoxide, II. 682d  
**Bloom**, II. 25a  
 — of varnish films, IV. 83a  
**Blower**, laboratory, I. 611d  
 "Blow" in water gas manufacture, V. 489c  
**Blown** oils, II. 25a; IV. 90d  
**Blue**, Acetylene, Pure and Sky, I. 90c  
 —, Acid Alizarin, I. 206a  
 —, Alizarin, BB, I. 230b  
 —, —, GR, I. 205b, 230b, 393a, 405a  
 —, Alizanthrene Navy, I. 424d  
 —, Alizarin, I. 205a, 206a, 228d, 413d  
 —, —, ABS, I. 229a  
 —, —, Brilliant Pure, R, I. 232b  
 —, —, Direct, I. 231c  
 —, —, A, B, I. 407b, 406b  
 —, —, Indigo, J. 205b  
 —, —, S, I. 229b  
 —, —, Marine, RO., I. 232b  
 —, —, OCS, RBN, I. 207a  
 —, —, Pure, B, I. 231d, 397c  
 —, —, RR, I. 397a  
 —, —, Sky, I. 206a, 231d  
 —, —, B, I. 405d  
 —, Alkali, I. 233b  
 —, Anthracene, I. 205b, 213a, 227c  
 —, —, SWX, WR, I. 206a, 230b, 391d, 392a  
 —, Anthraquinone, SR, I. 232a, b, 397d, 405c  
 —, Antwerp, I. 449c; II. 25c  
 —, ashes, II. 25c  
 —, Azure, I. 583c; II. 25b; III. 218c  
 —, Basle, I. 578a  
 —, Berlin, II. 25c  
 —, billy, III. 349d  
 —, Black, Alizarin, I. 206a  
 —, — Alizarin, B, SB, I. 404d, 231d  
 —, —, Alizuroil, I. 231d  
 —, Blackley, II. 2d  
 —, Bremen, II. 25c

**Blue**, Bronze, II. 25c; III. 473b  
 —, Caledon, brands, I. 414d  
 —, —, Brilliant, 3G, RN, I. 415a, 420c  
 —, —, Dark, BM, G, 2R, I. 421c, 425c  
 —, Capri, II. 271b  
 —, Carbazole, II. 279b  
 —, Celestine, II. 442c  
 —, Cerulean, II. 25a  
 —, Chinese, II. 25c; III. 33a  
 —, Cyanone, G, 3G, RA, I. 423c, 424d  
 —, cobalt, I. 583c; II. 25a; III. 218c  
 —, Cyanine, III. 514c  
 —, Durindone, 4BC, VI. 452c  
 —, Egyptian, IV. 257c  
 —, Erweco Alizarin Acid, R, I. 230d  
 —, —, Esmerne, II. 199c  
 —, —, Fluorescent, V. 272d  
 —, —, Gallamine, I. 569b  
 —, Gas, III. 473b  
 —, Green, Celliton, B, I. 42d  
 —, —, Indanthrene, FFB, I. 423c  
**Blueground** rock, III. 575c  
**Blue** gum tree, II. 25b  
 —, Hydron, II. 280b  
 —, —, R, VI. 418c  
 —, Indanthrene, BCS, RK, I. 415a, b  
 —, —, 5G, R, I. 400d, 415b; 394d, 566d  
 —, —, 3GT and R, I. 400c  
 —, Indone, I. 576c  
 —, Janus, G, I. 570b  
 —, John, II. 25b, 215a; V. 283a, 281a  
 —, King's, II. 25b; II. 218c  
 —, lead, II. 25b  
 —, Leitch's, III. 514c  
 —, Leyden, II. 25b  
 —, Lime, II. 25c, 58a  
 —, Manganese, II. 25c  
 —, Marine, I. 227c  
 —, Matt, III. 218d  
 —, Methylene, adsorption by rice protein, II. 502d  
 —, Mineral, III. 473b  
 —, Monastral and Chrome Yellow, III. 112d  
 —, —, Fast, BS, I. v; III. 333a; VI. 429b  
 —, Monthier's, III. 472d, 473b  
 —, Mountain, II. 25c; III. 20c  
 —,  $\alpha$ -Naphthol, VI. 418b  
 —, Neutral, I. 575d  
 —, New, III. 219a  
 —, Nicholson's, I. 233b  
 —, Novazol Acid, I. 578a  
 —, Paris, II. 25c; III. 473b, c  
 —, Pinachrome, III. 516c  
 —, Prussian, II. 25c; III. 472c, d  
 —, —, in Brunswick Green, II. 119c  
 —, —, in celluloid, II. 444b  
 —, —, insoluble, III. 472d  
 —, —, soluble, III. 472c  
 —, Quinaldine, III. 516c  
 —, Quinzarin, I. 231c  
 —, Quinolone, III. 515a  
 —, Rimman's, III. 219a  
**Blues**, Acid, I. 120a  
**Blue**, Saxon, II. 25c  
**Blues**, Brilliant, I. 415a  
 —, Ionamine, I. 205c  
 —, —, Pure, R, G, I. 40c  
**Blue**, Soluble, II. 25c

**Blue**, Solway, I. 230c  
 —, —, B, I. 403b, 405a  
 —, —, R, I. 400b  
 —, —, Sky, B, I. 405d  
 —, —, Ultra, B, I. 407b  
**Blues**, Polar, I. 578a  
 —, Soledon, I. 429b  
**Blue**, Steel, III. 473b  
 —, stone, II. 25a  
**Blues**, Wool Fast, I. 577d  
**Blue**, Thénard's, I. 583c; II. 25a; III. 218c  
 —, Thionol, VI. 418a  
 —, Toluylene, I. 509a; VI. 467c  
 —, Turnbull's, III. 471d, 473a  
 —, —, insoluble, III. 473a  
 —, Ultramarine, in Jacquers, II. 473b  
 —, Verditer, II. 25c  
 —, vitrol, III. 357b  
 —, Williamson's, III. 473b  
**Blushing** of collodion, II. 408d  
**Blutmehl**, II. 21d  
**Blutwurst**, II. 21c  
**Boart**, or bort, I. 3d; II. 309d; III. 574d  
**Bobbinite**, IV. 463a, 553c  
**Bobbin** spinning, V. 117b, 120d, 121a  
**Bodenite**, II. 512a  
**Boehmite**, Böhmite, I. 284b, II. 25c; VI. 101b  
**Boer** manna, II. 482d  
**Bog-butter**, II. 25d  
**Bog-iron-ore**, II. 26a  
 —, —, for purifying coal gas, V. 401d  
 —, —, manganese, II. 26a  
 —, "Bohnalite," I. 253a  
**Bohn-Schmidt** reaction, I. 205b, 213c  
 "Boiled Keene's" plaster, II. 131a  
**Boiled** oils, IV. 91a  
**Boiling** pt., detn., micro-method, II. 634b  
**Boldin**, II. 26b  
**Boldine**, II. 26b  
**Boldogluin**, II. 26b  
**Boldo** leaves, II. 26b  
**Bole**, Bohemian, II. 26b  
 —, mineral, II. 26b  
**Bolognan** stone, II. 26c  
 "Bolognian phosphorus," I. 640c  
**Boloretin**, II. 26d  
**Bombicestrol**, II. 26d  
**Bombonnes**, bombonnes, III. 75c  
**Bombycetin**, V. 87b  
**Bombycin**, V. 87b  
**Bombyx mori**, II. 26d; IV. 123d; V. 80a  
 —, spp., V. 86a  
 "Bondersing," protection of metals, III. 393a  
**Bone**, II. 26d  
 —, ash, II. 28b; V. 67a  
 —, black, I. 152d; II. 28b, 311c  
 —, chur, II. 311c  
 —, earth, II. 28b  
 —, fat, II. 28b; VI. 23b  
 —, —, extraction, II. 28c; VI. 23b  
 —, fats in candles, II. 203d  
 —, oil, II. 28a, 29c  
 —, —, fatty, II. 29c  
**Bones**, dissolved, fertiliser, V. 66d, 73b

- Bones**, fertiliser, V. 68*d*  
 —, vitrified, V. 73*b*  
**Bone-Wheeler** apparatus, II. 67*c*  
**Bonne chauffe**, II. 63*d*  
**Bononian** stone, II. 26*c*  
**Booster** (explosive), IV. 485*a*  
**Boothite**, III. 357*b*  
**Boracic** acid (*see also* Boric acid; Boron), II. 35*b*, 46*d*  
 — or boric acid preservative, V. 303*a*  
**Boracite**, II. 30*b*, 35*b*, 48*d*  
**Boragine**, VI. 191*b*  
*"Boral,"* II. 30*c*  
**Boramide**, II. 43*c*  
**Boranes**, II. 40*d*  
**Borate**, copper, II. 48*c*  
 —, hexamethylenetetramine, II. 53*c*  
 —, magnesium chloro-, II. 48*d*  
 —, manganese, II. 48*d*  
**Borates**, ammonium, II. 48*b*  
 —, barium, II. 48*b*  
 —, calcium, II. 48*c*  
 —, detection, *see* Boric acid; Boron  
 —, lead, II. 48*c*  
 —, metallic, II. 47*d*  
 —, potassium, II. 48*d*  
 —, sodium, II. 48*d*  
**Borax**, II. 48*d*  
 — and boric acid, industrial uses, II. 50*d*  
 — beads, II. 548*b*  
 — for glassmaking, V. 550*d*, 561*a*  
 — in cements and plaster, II. 131*d*  
 —, mineral, II. 30*c*  
**Borax usta**, II. 49*d*  
**Bordeaux**, Algol, 3*B*, I. 420*b*  
 —, Alzarin, I. 206*a*, 213*a*, 226*b*  
 —, — Brilliant, R., I. 212*d*, 22*c*  
*"Bordeaux"* dyes, I. 226*c*  
**Bordeaux**, Indanthrene, B extra, I. 420*a*, 420*b*  
 — mixture, II. 30*d*  
**Boric** acid (*see also* Boron), II. 35*b*, 46*d*  
 —, antiseptic properties, II. 47*c*; V. 303*a*, 306*b*  
 —, catalyst for acetic acid production, II. 350*d*  
 — in anthraquinone reactions, I. 205*c*, 213*c*  
 —, complex compounds, II. 47*d*  
 —, detection and detn., V. 303*c*  
 — in butter, II. 167*d*  
 —, food, detection and detn., V. 303*c*  
 —, — industry, II. 51*a*  
*"Boric acid phosphors,"* II. 46*d*  
**Boric** anhydride, I. 50*c*; II. 46*a*  
 — oxide, II. 46*a*  
 — for glassmaking, V. 559*d*  
**Boride**, chromium, III. 110*b*  
**Borides**, metallic, II. 44*b*  
 —, rare earth, II. 44*c*  
**Borimide**, II. 43*c*  
**Borneo** — camphor or *d* — borneol, II. 30*d*  
 — Illipé nuts, II. 34*d*  
**Borneol**, amino-, II. 245*b*  
 — and isoborneol, II. 30*d*  
**Borneol** and isoborneol, technical oxidation to camphor, II. 258*b*  
 — carboxylic acid, II. 243*a*  
 —, dehydration, II. 238*d*, 427*d*  
 — from bornyl chloride, II. 252*d*  
 — in camphor oil, II. 249*b*  
 — castor, II. 419*d*  
 —, occurrence, I. 1*c*; III. 183*c*  
 — oil, II. 256*a*  
**Borneols** from camphor, II. 242*b*  
**Borneol**, synthetic, II. 240*d*  
**isoborneol**, II. 30*d*, 237*c*, 256*a*  
 —, synthetic camphor from, II. 256*b*  
**Borneo** tallow, II. 31*c*  
 — in cacao butter, II. 187*c*  
 — chocolate, III. 88*b*  
**Bornesitol**, II. 32*c*  
**Bornite**, II. 32*c*, 517*d*; III. 341*c*  
**Bornyl** acetate, occurrence, I. 1*c*  
 —, oxidation, II. 31*c*  
**Bornylamine**, conversion into camphene, II. 238*d*  
 —, formation, II. 243*d*  
**neoBornylamine**, formation, II. 243*d*  
**isoBornylaniline**, II. 258*c*  
**Bornyl**  $\alpha$ -bromisovalerate, II. 119*a*  
 — chloride and isobornyl chloride, II. 32*d*, 250*c*  
 —, conversion into camphene, II. 33*c*, 237*c*, 252*c*  
 — from pinene, II. 33*b*, 250*c*  
 —, hydrolysis, II. 252*d*  
 —, isomerisation, II. 254*a*  
 — dibromodihydrocinamate, I. 141*a*  
**Bornylene**, II. 33*c*  
**apoBornylene**, II. 34*a*, 240*c*  
***d*-Bornylene** — 3 — carboxylic acid, azide, IV. 318*c*  
 — 3-hydroxamic acid, IV. 318*d*  
**Bornylene** nitrosite, II. 33*c*  
**Bornyl** isovaleroylglycolate, II. 31*b*  
*"Bornyl"* and *"Bornyl"*, *New*, II. 34*b*  
**neoBornyl**, II. 34*b*  
**Boroacetic** acid in esterification of pinene, II. 258*a*  
*"Borocaines,"* I. 360*b*; II. 34*b*  
**Borocalcite**, II. 35*b*  
*"Borocarbon,"* II. 34*b*  
*"Borocarbonyl,"* I. 4*a*  
**Boroethyl**, IV. 356*d*  
**Boro-glycerine**, II. 34*c*  
**Boron** (*see also* Boric acid), II. 34*c*  
 — arsenate, II. 46*c*  
 — as trace element, I. 505*a*; II. 35*a*  
**Boronatrocalsite**, II. 35*b*  
**Boron** carbides, I. 4*a*; II. 44*c*, 281*a*  
*"Boron, crystalline,"* II. 36*b*  
**Boron**, detection, II. 52*b*, 167*d*, 547*d*, 567*d*, 581*d*; V. 303*c*  
 —, detn., II. 52*b*, 645*b*, 653*d*; V. 303*c*  
 —, —, gravimetric, II. 591*d*  
 —, drop reactions, II. 52*b*, *d*, 581*d*  
 — hydrides, II. 40*d*  
 — hydronitride, II. 43*b*  
**Boron** hydrosulphide, II. 45*b*  
 — isotopes, II. 37*c*  
 — monoxide, II. 45*c*  
 — nitride, formation, II. 38*a*  
 —, phosphorescent, II. 43*a*  
 —, prepn., II. 43*a*  
 — oxides, II. 45*b*  
 — phosphate, II. 46*c*  
 —, radioactive, II. 37*d*  
 — silicides, I. 4*a*; II. 45*b*  
 — suboxides, II. 45*b*  
 — sulphide, II. 45*b*  
 — tribromide, II. 44*a*  
 — trichloride, II. 43*d*  
 — trifluoride, II. 43*c*  
 — as alkylating agent, VI. 259*c*  
 — tri-iodide, II. 44*a*  
 — trioxide, II. 46*a*  
**Borosalicylate**, ethyl, II. 53*c*  
 — sodium, II. 53*c*  
*"Boroverlin,"* II. 53*c*  
*"Borsalyl,"* II. 53*c*; IV. 29*a*  
**Bort**, I. 3*d*; II. 309*d*; III. 574*d*, 578*b*  
*"Boryl,"* II. 53*c*  
*"Bosa,"* II. 53*c*, 488*c*  
**Bosch**, II. 53*c*  
*"Bostonite,"* II. 53*c*  
**Boswellinic** acid, II. 53*c*  
**Botany** Bay gum, I. 618*a*  
**Botryolite**, II. 229*d*  
**Bottle** gas, V. 480*b*  
 — automobile fuel, V. 481*c*  
 —, cal. val., V. 481*a*  
 —, liquefied, as solvent, V. 481*c*  
 — nose oil, II. 53*d*  
**Bouchardat's** reagent, I. 235*c*  
**Bouillon** noir, II. 53*d*  
**Boulangerite**, I. 439*d*; II. 53*d*  
**Bournonite**, I. 439*d*; II. 53*d*; III. 311*c*  
**B.O.V.**, II. 119*a*  
**Bovey** coal, II. 53*d*  
**Bowl** metal, I. 442*b*  
**Brabender** farinograph, II. 78*b*  
**Braga**, II. 53*d*  
**Braggite**, II. 54*a*  
**Bragite**, II. 512*c*  
**Brain** lipid, II. 54*a*  
**Bran**, II. 54*a*; IV. 597*a*  
**Brandeivin**, II. 62*d*  
**Brandy**, II. 62*d*  
**Brandywine**, II. 62*d*  
**Brannetwein**, II. 62*d*  
**Brass**, II. 66*d*  
 —, electrodeposition, IV. 270*b*  
*Brassica nigra*, *B. campestris*, II. 2*d*; IV. 334*c*  
**Brassicic** acid, II. 66*d*  
 —, di-iodo-, esters, II. 67*b*  
**Brassylic** acid, II. 67*a*  
**Braunite**, II. 67*b*  
**Brazilin**, II. 68*d*, 73*a*  
**isoBrazilin**, II. 73*b*  
**isoBrazilinbromohydrin**, II. 73*b*  
**isoBrazilinchlorohydrin**, II. 73*b*  
**isoBrazilin** salt, II. 73*a*  
**Braziletto**, II. 67*c*  
**Brazilic** acid, II. 69*d*  
**Brazilin**, II. 68*b*  
**Brazilinic** acid, II. 70*a*  
**Brazilin**, occurrence, II. 195*b*  
**Brazilite**, I. 585*b*; II. 67*c*  
**Brazil** lump, II. 102*a*  
 — nut oil, II. 67*c*  
 — nuts, II. 67*c*

- Brazilone**, anhydrotrimethyl-, II. 71b  
 —, deoxytrimethyl-, II. 71b  
 —, triacetyl-, II. 71a  
**Brazilwood**, II. 67d  
 — extract, B. liquor, II. 71b  
**Bread**, II. 74c  
 — fruit, II. 85d  
**Breezes**, II. 86a  
**Brein**, IV. 275c  
**Breithauptite**, I. 439d  
**"Brentamines,"** azine bases, IV. 231b  
**"Brenthols,"** IV. 133a, 134a, 228b, 231a  
**Brewing** (see also Alcohol; Amylase; Fermentation, alcoholic), II. 86a  
**Brewster**, definition, V. 516c  
**Brewsterite**, I. 631b  
**B.R.I.**, I. 190b  
**Brick oil**, III. 423c  
**Bricks** and clay products, II. 123c  
 —, sand-lime, II. 118d  
**Bridelia** bark, *B. montana*, II., 105b  
**Bright annealing**, VI. 331c  
**Brightness factor**, III. 297a  
**Brillouin zones**, VI. 283d  
**Brimstone**, II. 105d  
**Brine** evaporation in open pans, IV. 411c  
**Briquettes**, V. 360b  
**Britannia Metal**, I. 115d; II. 105d  
**British thermal unit**, V. 433d  
**Broadfield** plant in phosphate production, V. 72c  
**Broccoli**, II. 182b  
**Brochantite** (see also Putna), II. 106a; III. 360d  
**Brodie's reagent**, II. 309d  
**Brönner's acid**, II. 118d; IV. 206d  
**Brönsted relation**, VI. 252d  
**Bröggerite**, II. 106a  
**Bromal**, II. 106a  
**Bromalammonia**, II. 106b  
**Bromal diacetate**, II. 106b  
 — glycolate, II. 106b  
**Bromargyrite**, II. 107d, 181c  
**Bromates**, defn., gravimetric, II. 610b  
 —, volumetric, II. 610b, 657b  
 —, qualitative reactions, II. 577a  
**Bromazide**, I. 581b  
**Brombutol**, II. 106b  
**Bromcarnallite**, II. 390a  
**Bromellia**, II. 106b; V. 328c  
**Bromellite**, I. 685a; II. 106c  
**"Brometone,"** II. 106b, 171d  
**Bromic acid**, II. 117d  
 —, defn. and qualitative reactions, see under Bromates; Bromine.  
**Bromides**, detection and defn., see under Bromine; Halogen.  
 —, qualitative reactions, II. 577a  
**"Bromidine,"** IV. 22b  
**Bromine**, II. 106c  
 — as chlorine carrier, II. 353b  
 — chloride, II. 116d  
 — compounds, II. 116c  
 —, detection and defn., see also under Halogen.  
**Bromine**, detection of gaseous, II. 682a  
 —, defn., gravimetric, II. 600d  
 —, in hydrogenation analysis, VI. 362b  
 —, volumetric, II. 653d, 657c  
 —, drop reaction, II. 581d  
 — fluoride, II. 116d  
 —, oxidation of aldehydes by, II. 362b  
 — oxide, II. 116a  
 — pentafluoride, II. 117a  
 —, qualitative reactions, II. 576d  
**"Bromine salt,"** II. 117d  
**Bromine trihydride**, II. 116d  
**"Brominol,"** II. 118a  
**"Brominoleum,"** II. 118a  
**"Bromopin,"** II. 118a  
**Bromite**, II. 107d, 118b  
**Bromobehenate**, II. 118b  
**Bromoform**, II. 118b  
 —, chloro-, II. 118b  
**Bromol** photographic prints, III. 111a  
**"Bromophin,"** II. 118c; IV. 401d  
**"Bromopin,"** II. 118a  
**Bromoprene**, I. 89d; II. 155d  
**Bromostyrol**, II. 118c  
**Bromsulphthalein**, II. 118d  
**"Bromural,"** II. 118d  
**Bromyrite**, II. 118b  
**Bronze**, Cobalt, I. 219b  
 — powders, II. 118d  
**Bronzite**, IV. 311a  
**Brookite**, I. 370a; II. 119a  
**Broom corn**, II. 182c  
***Brosimum galactodendron***, II. 119a  
**Brouillis**, II. 63d  
***Broussonetia papyrifera***, II. 119a  
**"Brovalol,"** II. 119a; IV. 389b  
**Brown acid**, II. 119a  
 —, Alizarin, I. 228c  
 —, Anthracene, I. 212d  
 —, —, FI, see Anthragallol.  
 —, berries, II. 119a  
 —, Bismark, I. 238a; IV. 200a, 226a  
 —, Cacao, II. 188a  
 —, Caledon, R., I. 422c; II. 119b  
 —, Caledonian, II. 119a  
 —, Cappagh, II. 119a  
 —, Catechu, II. 133c  
 —, Chbanone, B., I. 423c; II. 119a  
 —, Cobalt, III. 219c  
 —, G.R.B.R., I. 116d; II. 119b  
 —, Hatched's, III. 171a  
 —, Indanthrene, Blt and GR, I. 421b, d  
 —, Indigo, VI. 437a, 438d  
 —, iron-ore, VI. 191a  
 —, Leather, I. 133b  
 —, oil, III. 245d  
 —, ore, II. 519d  
 —, red antimony sulphide, I. 446c  
 —, spar, IV. 53d  
 —, Vandyke, II. 119a, 418b  
**Brucine**, II. 119b  
 —, nitro-deriv., II. 188c  
 —, occurrence, II. 182a  
**Brucite**, II. 119b  
**Brugères powder**, IV. 483b  
**Brunner's salt**, II. 119b  
**Brushite**, II. 119c  
**Brussels sprouts**, II. 119c, 182b  
**Bryogenin**, II. 119d  
**Bryoidin**, II. 119c; IV. 275b  
**Bryon**,  $\alpha$ - and  $\beta$ -, II. 110d  
**Bryonin**, II. 119d  
**Bryonol**, II. 119d  
**Bryony root**, II. 119c  
**B.Th.U.** or British thermal unit, V. 331c, 433d  
**Bucco**, II. 119d  
**Buchu**, II. 119d  
 —, camphor, II. 120c; IV. 8c  
 —, essential oil, II. 120a  
**Buckthorn**, II. 120c  
**Buckwheat**, II. 120c  
**Buflagin**, II. 120b, 388c  
**Buffer solutions**, II. 120b; VI. 337c  
**"Buffer solution, universal,"** II. 123a; VI. 337c  
**Buff stone**, III. 32c  
**Bufothalen**, II. 388b  
**Bufothalin**, II. 388a  
**Bufothenidin**, II. 388a  
**Bufothenine**, II. 387d; VI. 463c  
**Bufothionin**, II. 388a  
**Bufo toxin**, II. 388a  
**Bugloss**, Languedoc, I. 230d  
**Buhrstone**, I. 4b; II. 150d  
**Building materials**, II. 123b  
 — stone, II. 137c  
**Bulbocapnine**, II. 150c  
**Bultfonteinite**, II. 150c  
**Bung-hole** boiled oil, IV. 91b  
**Buntkupfererz**, II. 32d  
**Bupleurol**, II. 150c  
**Burgundy pitch**, II. 261b  
**Burkheiser's process**, I. 311b  
**Burnite**, I. 302c  
**Burning bush**, IV. 400c  
 — in cement manufacture, II. 133d  
**Burrstone**, I. 4b; II. 150d  
**Burrs**, wool removal, II. 11b  
**Bush salt**, II. 150d  
**Buszite**, II. 150d  
**Butadiene**, II. 150d  
 — 2-acetoxy-, I. 88b  
 —,  $\beta$ -formyl-, I. 89b  
**zy-Butadiene** from acetylene, I. 85b  
 —  $\alpha$ -butylene, II. 177b  
 — catechol, II. 430c  
**Butadienes** and polyolefins, II. 151d  
 —, bromo-, I. 89d; II. 154b  
 —, chloro-, and dichloro-, I. 89a; II. 151b  
 —, conjugated, II. 151a  
 —, non-conjugated, II. 156b  
**Butaldehyde**, bromo-, prepn., II. 169d  
**isoButaldehyde**, bromo-, II. 170d  
**Butaldehyde**,  $\beta$ -chloro-, ethyl acetal, I. 36b  
 — dibutyl acetal, mono- and dichloro-, II. 170b  
 —,  $\beta$ -ethoxy-, ethyl acetal, I. 36b  
 —,  $\beta$ -hydroxy-, I. 26b, 198a  
**Butaldehydes**, II. 156d  
**Butaldehyde**,  $\beta\beta$ -trichloro-, II. 157b; III. 35d  
 —, chloro-, II. 170c  
**Butane**, II. 173a; V. 480b  
**cycloButane**, II. 173b  
**isoButane**, II. 173b  
**n-Butane**,  $\alpha$ -amino- $\delta$ -guanido-, I. 171c

- Butane** as fuel, II. 157b  
 — — refrigerant, II. 173b  
 — —  $\alpha$ -bromo, II. 171c  
 — —  $\alpha$ -chloro-, II. 172a  
 — — diamino-, II. 178c  
 — — dibromo-, II. 171d, 177d  
 — — in carburetted water gas manufacture, V. 472b  
 — — nitrohydroxy-, II. 171c  
**Butanes**, II. 173a  
 — — dihydroxy-, II. 178d  
 — — nitro-, II. 171b  
**Butanol**, *see* *n*-Butyl alcohol.  
**2-Butanone** or methyl ethyl ketone, I. 71a; II. 472b  
*Butea frondosa*, II. 157d; VI. 80c  
**Butein**, II. 74b, 158b  
 — — tetra-acetyl-, II. 158b  
 — — trimethyl ether, II. 73d  
*"Butesin,"* II. 159b  
**Butin**, II. 158a  
*"Butolan,"* II. 159b  
*"Butoxyl,"* II. 159b  
**Butrin**, VI. 80c  
**Butter**, II. 159b  
 — — colouring matters, II. 167c  
 — — diacetyl in, V. 306a  
 — — fat, composition, II. 161b  
 — — formation from milk fat, II. 160d  
 — — mineral, II. 168d  
 — — nuts, II. 168d  
 — — substitutes, IV. 253b  
 — — vegetable, II. 159c, 168d; III. 242a  
 — — vitamins, II. 163d  
**Buttgenbachite**, II. 168d  
**Button lac**, II. 169a  
**Butyl**, II. 169a  
*n*-Butylacetal, I. 36a  
*iso*-Butylacetal, I. 36a  
**Butyl** acetate in lacquers, II. 471d  
 — — specification, II. 472b  
*iso*-Butylacetic acid, II. 271b  
*iso*-Butylacetooacetic acid, ethyl ester, I. 64c  
*n*-Butyl alcohol, I. 27d; II. 169a  
*iso*-Butyl alcohol,  $\beta$ -chloro-, II. 178b  
*sec*-.Butyl alcohol, 1-chloro-, II. 177b  
*iso*-Butyl alcohol from carbon monoxide and methanol, II. 350d  
*n*-Butyl alcohol from crotonaldehyde, I. 26c, 27d  
**Butyl** alcohol from horse-chestnuts, VI. 279d  
 — — in lacquers, II. 169b, 471d  
 — — production, II. 27d; I. 169b, 426d, 429b, 471d; V. 45b  
 — — alcohols, II. 169a  
 — — alcohol, specification, II. 472b  
*tert*-.Butyl alcohol, tribromo-, II. 106b  
 — —,  $\alpha\alpha\alpha$ -trichloro-, I. 70c, 371c; III. 36c  
**Butylamines**, II. 175c  
*n*-Butyl *p*-aminobenzoate, II. 159b  
*iso*-Butyl *p*-aminobenzoate, III. 535d  
*n*-Butyl bromide, II. 171c  
*iso*-Butyl bromide, II. 170d  
*n*-Butyl butyrate, II. 179c  
*iso*-Butyl isobutyrate, II. 170d  
*iso*-Butylcarbinol, I. 358c  
*sec*-.Butylcarbinol, I. 359a  
*tert*-.Butylcarbinol, I. 359b  
*"Butyl carbitol,"* II. 179b  
*"Butyl cellulosolve,"* II. 179b  
**Butyl** chloral, II. 157b; III. 35d  
 — — hydrate, II. 179b; III. 35d  
 — — chloride, II. 172a  
*iso*-Butyl  $\alpha$ -chloroisobutyrate, II. 170d  
**Butyl** compounds, *n*-, *iso*-, *sec*-, and *tert*-, *see also* Butyl.  
**Butylcresol**, II. 171d  
**Butyl** cyanate, II. 172c  
 — — cyanide, II. 172d  
 — — derivs. of aryl nitro-compounds, II. 174c  
 — — diselenide, II. 175b  
*iso*-Butyl disulphide, II. 175b  
*iso*-Butylene bromide, II. 171c  
*ψ*-Butylene, bromo-, II. 177c  
**Butylene** bromohydrin, II. 178c  
 — — diamines, II. 178c  
 — — dibromide, II. 177d  
*iso*-Butylene dicyanide, II. 178b  
**Butylene** di-iodide, II. 179a  
*iso*-Butylene dinitrite, II. 179a  
 $\beta$ -Butylene from butyl alcohol, II. 160d  
**Butylene** glycolchlorohydrin, II. 178b  
**1:3-Butylene** glycol ether acetate, II. 159b  
**Butylene** glycols, II. 178d  
 — — oxide, II. 179b  
*iso*-Butylene oxide, IV. 320c  
 — —, chloro-, IV. 320c  
**Butylenes**, II. 176d  
**Butyl** esters, II. 170a  
*iso*-Butyl ether,  $\alpha\beta$ -dichloro*iso*-butyl-, II. 170c  
**Butyl** ethers, II. 174d  
*iso*-Butylformal, I. 34b  
**Butyl** iodide, II. 173c  
 — — mercaptans, II. 174a  
 — —, metallic derivs., II. 173c  
 — — nitrates, II. 174b  
 — — nitrites, II. 174b  
 oleate in lacquers, II. 472d  
 — — phthalate in lacquers, II. 468b  
 — — stearate in lacquers, II. 479a  
 sulphides, II. 175a  
 — — sulphone, II. 175a  
 — — tartrate in lacquers, II. 470b  
 — — telluride, II. 175b  
 — — isothiocyanates, II. 175b  
*m*-*tert*-.Butyltoluene, II. 174c  
 — —, trinitro-, II. 174c  
**Butylxylene**, II. 174d  
*"Butyn,"* I. 369a; II. 179b  
**Butyramide**, II. 180c  
*iso*-Butyramide, II. 181b  
**Butyrates** in carrot seed oil, II. 404b  
*iso*-Butyric acid, II. 180d, 362a  
**Butyric** acid, *d*-amino-, I. 317a  
*iso*-Butyric acid,  $\alpha$ -bromo-, II. 181b  
**Butyric** acid,  $\beta$ - and  $\gamma$ -bromo-, II. 180c  
*iso*-Butyric acid,  $\alpha$ -chloro-, II. 181b  
**Butyric** acid,  $\beta$ - and  $\gamma$ -chloro-, II. 180c  
 — —,  $\beta$ -hydroxy-, VI. 401d  
 — — in butter fat, II. 182c  
 — — acids, *n*- and *iso*-, II. 179c  
**Butyric** aldehyde, trichloro-, II. 157b; III. 35d  
 — — anhydride, II. 180c  
*iso*-Butyric anhydride, II. 181b  
 — — esters, II. 181b  
 $\gamma$ -Butyrobetaines, I. 687a  
**Butyrolin**, I. 140c  
 $\gamma$ -Butyrolactone, II. 181d  
**Butyrolactone- $\gamma$ -carboxylic** acid, VI. 39b  
**Butyrone**, II. 181d  
 — — pinacone, II. 181d  
 $\gamma$ -Butyrottrimethylbetaine from carnitine, II. 391b  
**Butyryl** chloride, II. 180b  
*iso*-Butyryl chloride, II. 181a  
**Buxine**, II. 181d  
*Buxus sempervirens*, alkaloids, II. 182a  
**Byssochlamic** acid, V. 56b  
*Byssochlamys fulva* in fermentations, V. 51c  
**Byssus**, II. 182c  
**Bytownite**, I. 652a; V. 3a  
  
*"Caapi,"* II. 182a; VI. 186a  
 Caapi alkaloids, II. 182a  
**Cabalonga** de Tabasco, II. 182a  
**Cabbage**, II. 182a  
 — — acids, II. 182d  
**Cacao** butter or cocoa butter, II. 168d, 183d; III. 233b  
 — —, acids, II. 185c  
 — —, adulteration, II. 185b, 187a  
 — — or cacao fat, German regulations, II. 184a  
 — — germ fat, II. 186b  
 — —, "liquid nib," II. 184b  
 — — mass, II. 184b  
**Cacaorin**, II. 188a  
**Cacao** shell, IV. 597a  
 — — fat, II. 186b  
 — — tree, II. 183d; III. 230d  
**Cachalot** oil, II. 188b  
**Cachou** de Laval, II. 188b  
**Cacodyl** and its derivs., I. 480d  
**Cacodyl** carbide, I. 481b; II. 188b  
*"Cacodyliacol"* or *"Cacodyliacogol,"* II. 188b  
**Cacodylic** acid, I. 481b; II. 188b  
**Cacodyl** oxide, I. 480a; II. 188c  
**Cacotheline**, II. 188c, 581b  
**Cacouatl**, III. 230d  
**Cadaleine**, II. 188c, 190a, b  
**Cadaverine**, II. 188c  
 — — in ergot, IV. 331d  
**Cadechol**, II. 188c  
**Cade** oil, II. 188c  
**Cadet's** "fuming liquid," I. 470d; II. 188c  
**Cadinene**, I. 5c; II. 188c  
 — —, dehydrogenation, II. 188c, 190a  
 — — dihydrochloride, III. 337c  
 — — from copaene, II. 190a  
 — —, in camphor oil, II. 249c  
*iso*-Cadinene, II. 190a  
**Cadinol**, II. 190b  
**Cadmia**, II. 201b  
**Cadmium**, II. 190c  
 — — chloride, II. 193d  
 — — cyanide, II. 194d



- Cadmium**, detn., by hydrogenation, VI. 361*d*  
 ---, electrodeposition method, II. 700*c*  
 ---, ---, gravimetric, II. 590*b*  
 ---, ---, in hydrogenation analysis, VI. 362*a*  
 ---, ---, spectroscopic, II. 692*a*  
 ---, ---, volumetric, II. 654*a*  
 ---, drop reactions, II. 580*a*  
 ---, electrodeposition, IV. 268*c*  
 ---, hydroxide, II. 193*d*  
 ---, iodide, II. 194*a*  
 ---, lithopone, II. 194*d*  
 ---, monoxide, II. 193*c*  
 ---, nitrate, II. 194*d*  
 ---, peroxide, II. 193*d*  
 ---, phosphate, polymerising agent, II. 429*a*  
 ---, pigments, II. 194*b*  
 ---, qualitative reactions, II. 551*d*, 567*c*  
 ---, ---, rare metals present, II. 555*b*, 556*d*  
 ---, salicylate, II. 194*d*  
 ---, suboxide, II. 193*d*  
 ---, sulphate, II. 194*c*  
 ---, sulphide, II. 194*a*  
 ---, ---, mineral, II. 190*d*  
**Cadmopone**, II. 194*b*  
**Cæline**, III. 219*a*  
**Cæruleoellagic acid**, II. 194*d*  
**Cæruleum**, III. 219*a*  
**Cæruleum montanum**, I. 583*d*  
**Cæsalpinia brevifolia**, tanning extract, I. 201*b*  
 ---, *coriaria*, divi-divi, IV. 52*d*  
 ---, *sappan*, II. 195*b*  
 ---, *spp.*, ellagic acid sources, IV. 276*d*  
 ---, ---, tannins from, IV. 276*d*  
**Cæsium**, II. 195*b*  
 ---, as trace element, I. 505*c*  
 ---, beryl, I. 684*c*  
 ---, chloride, II. 190*c*  
 ---, detn., gravimetric, II. 585*a*  
 ---, hydride, II. 190*c*  
 ---, hydroxide, II. 190*b*  
 ---, monoxide, II. 190*c*  
 ---, peroxide, II. 190*c*  
 ---, qualitative reactions, II. 547*c*, 554*a*, 556*d*, 566*b*  
 ---, sulphate, II. 190*c*  
**Caffearine**, II. 196*d*  
**Caffeic acid**, II. 196*d*  
**Caffeine** and the alkaloids of tea, coffee and cocoa, II. 197*a*; III. 254*b*  
**Caffeol**, II. 198*b*  
**Caffeone**, II. 198*b*  
**Caffetannic acid**, II. 198*b*; III. 79*d*, 254*b*  
**Cahucit**, IV. 463*b*  
**Caill-Cedra**, II. 198*b*  
 ---, cedrin, II. 198*b*  
**Cairngorm**, II. 198*c*  
**Calisson** disease, *see* "Divers' bends."  
**Cajuput**, essential oil, II. 198*c*  
**Cajuputol**, *see* 1:8-Cineole and Cineole.  
**Cal**, II. 198*d*  
**Calabar bean**, II. 198*d*  
**Calabarine**, II. 200*b*  
**Calafatite**, I. 298*a*  
**Calamene**, II. 200*d*  
**Calameneae**, II. 201*a*  
**Calamenol**, II. 201*a*  
**Calameon**, II. 201*a*  
**Calameonic acid**, II. 201*a*  
**Calamine**, VI. 202*a*  
 ---, electric, II. 201*b*  
 ---, in pharmacy, II. 201*b*  
 ---, minerals, II. 201*a*  
**Calamus, acorus**, I. 124*b*  
 ---, essential oil, I. 121*b*  
**Calandra granaria**, *C. spp.*, V. 392*d*, 395*c*  
**Calandria** of vacuum pans, IV. 406*b*  
**Calaverite**, II. 201*c*; VI. 102*a*  
 "Calciobronat," II. 201*c*  
 "Calcidine," II. 201*c*  
**Calciferol**, II. 201*c*; III. 249*b*  
 "Calcinol," II. 203*b*  
 "Calcicoramine," II. 203*b*  
**Calcite**, II. 203*b*, 220*a*, 518*a*  
**Calcium**, II. 203*d*  
 ---, acetylide - acetylene - am - monin, II. 215*d*  
 ---, alloys, II. 205*b*  
 ---, aluminate, II. 228*b*  
 ---, amide, II. 222*b*  
 ---, ammonium, II. 222*a*  
 ---, ferrocyanide, III. 470*d*  
 ---, arsenate, II. 226*b*  
 ---, azide, II. 222*a*  
 ---, borate, II. 229*d*  
 ---, boride, II. 229*c*  
 ---, bromide, II. 211*c*  
 ---, urethane, double salt, II. 235*a*  
 ---, camphorate, camphorone from, II. 260*c*  
 ---, carbide, II. 215*d*, 280*d*  
 ---, acetylene production from, I. 107*b*  
 ---, in bread analysis, II. 82*c*  
 ---, storage, I. 109*b*  
 ---, carbonate, II. 203*b*, 220*a*, 518*a*  
 ---, decomposition, II. 220*b*, 324*c*, 537*c*  
 ---, for glassmaking, V. 500*a*  
 ---, in caramel prepn., II. 276*b*  
 ---, carbonyl, II. 357*c*  
 ---, chlorate, II. 211*b*  
 ---, chloroarsenate, II. 227*a*  
 ---, chlorosilicate, II. 228*a*  
 ---, chromate, II. 231*a*; III. 103*b*, 111*d*  
 ---, citrate, III. 186*a*, 190*a*  
 ---, compounds for glassmaking, V. 500*a*  
 ---, cyanamide, II. 219*c*; III. 505*c*; V. 65*c*  
 ---, formation, II. 216*a*  
 ---, cyanide, III. 492*b*  
 ---, deficiency, treatment, II. 207*b*  
 ---, detn., gravimetric, II. 588*c*  
 ---, in clay, III. 203*a*  
 ---, ---, volumetric, II. 651*c*  
 ---, dioxide, II. 212*b*  
 ---, disulphide, II. 230*c*  
 ---, drop reaction, II. 580*b*  
 ---, ferrocyanide, III. 468*a*, 470*c*  
 ---, fluoride, II. 215*a*  
 ---, gluconate, II. 201*c*, 234*a*, 297*b*  
 ---, hydride, II. 205*d*, 685*d*  
 ---, hydrogen carbonate, II. 220*d*  
 ---, hydrosulphide, II. 230*c*  
 ---, hydroxide, II. 211*d*  
 ---, hydroxy - sulphhydrate, II. 231*b*  
 ---, hypochlorite, III. 63*b*  
 ---, hypophosphite, II. 223*c*  
 ---, imide, II. 222*b*  
**Calcium** in cabbage, II. 183*a*  
 ---, in plants, I. 505*c*  
 ---, iodate, II. 203*b*, 214*d*  
 ---, iodide, II. 201*c*, 214*d*  
 ---, mercuride, II. 205*a*  
 ---, metaphosphate, II. 226*a*  
 ---, monosulphide, II. 229*d*, 271*a*  
 ---, nitrate, II. 222*c*  
 ---, nitride, II. 204*d*, 221*d*  
 ---, nitrite, II. 222*b*  
 ---, oxalate in wort, II. 90*a*  
 ---, oxide, II. 200*b*  
 ---, reaction with CO and steam, II. 349*b*  
 ---, oxychloride, II. 214*a*  
 ---, oxysulphide, II. 230*d*  
 ---, pentasulphide, II. 230*c*  
 ---, perchlorate, II. 214*c*  
 ---, periodate, II. 215*a*  
 ---, pernitride, II. 222*a*  
 ---, persulphate, II. 233*d*  
 ---, phosphate, II. 119*c*, 204*a*, 223*d*  
 ---, acid, in flour, II. 81*c*  
 ---, complex with casein, II. 411*b*  
 ---, in bone ash, II. 28*b*  
 ---, in flour, II. 79*c*  
 ---, phosphato-chlorides, II. 220*a*  
 ---, phosphide, II. 223*b*  
 ---, phosphate, II. 223*c*  
 ---, acid, II. 223*c*  
 ---, potassium chromate, II. 231*a*  
 ---, ferrocyanide, III. 470*d*  
 ---, sulphate, II. 233*c*  
 ---, pyrophosphate, II. 225*d*  
 ---, qualitative reactions, II. 553*d*, 567*a*  
 ---, ---, rare metals present, II. 555*d*, 556*d*  
 ---, rôle in blood clotting, II. 23*c*  
 ---, saccharate, II. 212*a*  
 "Calcium-Sandoz," II. 234*a*  
**Calcium selenide**, II. 232*a*  
 silicate, electrolysis, II. 227*a*  
 silicates, II. 227*c*  
 silicide, II. 227*a*  
 silicoborate, II. 220*d*  
 silicophosphate, II. 220*b*  
 silicotitanate, II. 229*d*  
 silver iodide, II. 214*d*  
 sodium sulphate, II. 233*c*  
 sulphate (*see also* Gypsum), II. 232*b*  
 ---, hemihydrate, II. 130*a*  
 ---, sulphate in ammonium sulphate production, II. 424*b*  
 ---, ---, masonry, II. 128*c*  
 ---, ---, mineral, II. 204*a*  
 ---, ---, plasters and cements, II. 129*b*  
 sulphite, II. 232*a*  
 sulphocarbonate, II. 231*d*  
 tetroxide, II. 212*c*  
 thiocyanate, II. 203*b*  
 thiosulphate, II. 233*d*  
 titanate, II. 220*d*  
 ---, zirconate, II. 420*c*  
**Calco-uranite**, I. 558*a*; II. 393*a*  
**Calc-spar** (*see also* Calcite), II. 203*b*  
**Calculations**, chemical, III. 1*a*  
**Caldariomycin**, V. 58*c*  
 "Caledon" dyes, I. 424*b*  
**Calendering** textiles, V. 188*a*  
**Calendula officinalis**, II. 234*a*  
**Calgon**, II. 234*b*  
**Calitaur wood**, II. 234*b*

- Caliche**, II. 234b  
**Calico** printing, IV. 178d  
 —, casein in, II. 411b  
 —, direct styles, IV. 179a  
 —, dyed styles, IV. 181c  
 —, with aniline black, IV. 179c  
 —, azoic dyes, IV. 182a  
 —, "Rapidazol" dyes, IV. 183c  
 —, "Rapidogen" dyes, IV. 183a  
**Californite**, II. 234b  
 "Calines," caulocaline, phyllo-caline, rhizocaline, VI. 138c  
**Calisaya**, II. 234b  
**Callaita**, I. 261d  
**Callistephin**, II. 234b  
**Callistephus chinensis**, I. 532d  
**Callitris glauca**, VI. 142b  
 —, *infratropica*, VI. 142b  
**Callitropic acid**, II. 234d  
**Calluna vulgaris**, II. 231d; IV. 333b; VI. 190a  
**Callutannic acid**, II. 234d  
**Calmatambetin**, II. 235a  
**Calmatambin**, II. 235a  
 "Calmonal," II. 235a  
 "Cal-nitro," I. 352d  
**Calomel**, *detm.*, II. 662d  
 —, half-element, VI. 336a  
 "Calomelol," II. 235a  
**Caloncoba glauca**, *C. spp.*, II. 235a  
**Calophyllum inophyllum**, II. 235a  
**Calophyllum oil**, II. 235b  
 —, fatty acids, II. 235b  
**Caloric** values, gross and net, V. 331d  
 —, of fuels, V. 331c  
**Calotropis spp.**, V. 169b  
**Calotype**, II. 235b  
**Calumba** alkaloids, II. 235b  
 "Caluados," III. 127c  
**Calycanthine**, *isoculycanthine*, II. 236c  
*Calycanthus spp.*, II. 236c  
**Cambe** wood, II. 260c  
**Camboge**, III. 237a; V. 427c  
**Cambrite**, IV. 653c, 551c  
**Camellina sativa**, II. 237b  
**Cameline oil**, II. 237a  
**Camellia japonica**, VI. 86c  
**Camellia-saponin**, VI. 86c  
**Campeachy wood**, II. 237b  
**d-Camphane-3-carboxylic acid**, IV. 318c  
**Camphane**,  $\alpha$ -dichloro-, II. 239b  
*isoCamphane* formation, II. 242b  
**Camphene**, II. 237c, 252c  
 —,  $\omega$ -bromo-, II. 238b  
 —,  $\omega$ -chloro-, II. 239b  
 —, from borneol, II. 31c  
 —, bornyl chloride, II. 252b  
 —, pinene, II. 258b  
 —, glycol, II. 239a  
 —, hydrate, II. 238c  
 —, hydrochloride, II. 239c  
 —,  $\omega$ -nitro-, II. 239c  
 —, oxidation, II. 240d  
 —, oxidation to camphor, II. 238d, 257a  
 —, source of borneol, II. 31b  
**Camphenic acid**, II. 238a  
**Camphenilol**, II. 240c  
**Camphenilone**, II. 237d, 240a  
 —, formation, II. 257b  
**Camphenyl chloride**, II. 240c  
 —, methyl, xanthate, distillation of, II. 34a  
**Camphenylic acid**, II. 238b  
 —, nitrite, II. 239c  
**Camphochol**, II. 240c  
**Camphol**, II. 240d  
 **$\alpha$ -Campholenaldehyde**, II. 242b  
**Campholene** formation, II. 243d  
 **$\alpha$ -Campholenic acid**, dihydro-, II. 244b  
**Campholic acid**, II. 241a  
*isoCampholic acid*, II. 244a  
 **$\alpha$ -Campholide**, II. 242b, 247d  
 **$\beta$ -Campholide**, II. 247d  
 **$\alpha$ -Campholytic acid**, II. 248c  
**Camphonenic acid**, II. 249a  
**Camphor**, II. 240d  
 **$\beta$ -Camphor**, IV. 318c  
**Camphor**, acetyl-, II. 243c  
 —, amino-, II. 245b  
**Camphoranil**, II. 258c  
 "Camphor, artificial," II. 32d, 250c  
**Camphor**, benzoyl-, II. 243c  
 —, carboxylic acid, II. 243a  
 —, chloro-, II. 244b  
 —, compound with apocatheic acid, II. 240c  
 —, —, deoxychoic acid, II. 188c  
 —, dehydration, II. 401c  
 —, derivs., numbering, II. 243c  
 —, *detm.*, II. 259d; IV. 533c  
 **$\alpha$ -Camphorene** in camphor oil, II. 249c  
**Camphor**, essential oil, II. 249b  
 —, from borneols, II. 31c, 256b  
 —, glycol, II. 246d  
 —, halogen derivs., II. 244b  
 —, hydroxy-, II. 245d  
**Camphoric acid**, II. 241a, 247c  
 —, —,  $\beta$ -bromo-, II. 248b  
 —, formation, II. 33c, 31a  
 —, hydroxy-, II. 237b  
*apoCamphoric acid*, II. 239a, 241c  
 —, —, carboxy-, II. 239a  
*cis-apoCamphoric acid*, II. 34b  
*isoCamphoric acid*, II. 247c  
**Camphoric anhydride**,  $\alpha$ -bromo-, II. 248b  
 —, —,  $\alpha$ -chloro-, II. 248b  
**Camphorimide**, II. 248a  
**Camphor** in celluloid, II. 249c, 260a, 413b  
 —, iodo-, II. 244d  
 "Camphor, Ngau," II. 30d  
**Camphor**, nitro-, II. 245a  
 —, pseudonitro-, II. 245a  
 —, isonitroso-, II. 246c  
**Camphorone**, II. 260c  
**Camphoronic acid**, II. 241b, 242b, 248a  
*isoCamphoronic acid*, II. 242b  
**Camphorquinone**, II. 246c  
 —, reduction, II. 245d  
**Camphorsulphonic acids**, II. 245c  
**Camphor**, synthetic, II. 249c  
 "Camphotar," IV. 31a  
**Camphylic acid**, II. 248c  
**Camwood**, II. 260c  
**Canada balsam** and resin, II. 261a  
 —, in flexible collodium, II. 468c  
 —, pitch, II. 261b  
 "Canada Snake-root," I. 498d  
**Canadine**, II. 261b; VI. 295c  
**Canadolic acid**, II. 261b  
**Canadolinic acid**, II. 261a  
**Cananga**, essential oil, II. 261b  
**Canarin**, II. 261b  
**Canarium spp.**, IV. 275a, 276a  
*Canavalia ensiformis*, I. 659a  
**Canavanine**, I. 318b  
**Cancer**, experimental production, II. 378b  
**Candelilla wax**, II. 261c  
**Candle** making, VI. 222c  
**Candlenut**, II. 262b  
 —, oil, I. 198c; II. 262b  
**Candles**, II. 263a  
 —, dyes for colouring, II. 268d  
 —, tallow, acrolein from burning, II. 263c  
**Candle** wicks, borax pickling, II. 50d, 265a  
**Canella alba**, II. 269c  
**Canella bark**, II. 269c  
 "Canellin," II. 269c  
**Canfieldite**, I. 160c; V. 520c  
**Canabinol**, II. 269d  
**Canabinolactone**, II. 269d  
**Cannabis indica** resin, II. 269c; VI. 422c  
 —, *sativa*, I. 1a; IV. 86a, 251b; V. 162c; VI. 205a, 422c  
 —, protein, IV. 251b  
**Canna caldis**, I. 168b  
**Cannel** coal and coke, V. 437c  
**Canning** and bottling, V. 290b  
**Cannizzarite**, II. 270a  
**Cannizzaro's reaction**, II. 270a  
**Cannonite**, IV. 533a  
**Cannon-spar**, II. 263c  
**Cans**, corrosion and protection, V. 290c  
**Cantharides**, II. 270b  
**Cantharidic acid**, II. 270b  
**Cantharidin**, II. 270b  
 —, containing insects, II. 271a  
*isoCantharidin*, II. 271a  
*Cantharis vesicatoria*, II. 270b  
**Canthium glaberrimum**, II. 235a  
**Canton's phosphorus**, II. 230a  
**Canvas** roofing, V. 145d  
**Caoutchouc**, *see* Rubber.  
**Cap** compositions, IV. 543c  
 "Cape ruby," V. 129c  
**Capric acid**, I. 199c; II. 271b; IV. 278c  
**Caprine**, II. 271b  
**Caproic acids**, II. 271b  
 —, —,  $\alpha$ -amino-, III. 317a  
 **$\psi$ -Caproic acid**, II. 271c  
*isoCaproic acid*, II. 271d  
**Caproic acids**, II. 271b  
 "Caprokol," II. 271d  
**Capryl** or octyl, II. 271d  
**Caprylic acid**, I. 199c  
**Capsaicin**, II. 271d, 271c  
**Capsanthin**, II. 272b, 399b  
**Capsanthinone**, II. 273a  
**Capsanthol**, II. 273c  
**Capsanthylal**, II. 273b  
**Capsicine**, II. 275b  
**Capsicum**, II. 273b  
 —, resin, II. 275b  
*Capsicum spp.*, II. 271d, 272b, 275b  
**Capsorubin**, II. 272b, 399b, 401a  
**Capsularigenin**, II. 275c  
**Capsularin**, II. 275c  
**Capsylaldehyde**, II. 273a

- Caput mortuum*, II. 275c; III. 278c
- Carajura*, I. 381d; II. 275c; III. 28b
- Carajuretin*, II. 275c
- Carajurin*, II. 275c; III. 28c
- , dibromo-, III. 28d
- Carajurone*, II. 275d; III. 28c, 29c
- Carambola*, II. 275d
- Caramel*, II. 276a
- Caramelan*, II. 276c
- Caramel*, detn., II. 277a
- Caramelen*, II. 276c
- Caramelic acid*, II. 276c
- Caramelin*, II. 276c
- Carana*, II. 277b
- Carane*, II. 388d
- Carapa oil*, II. 277b
- Caratol*, in carrot seed oil, II. 404b
- Caraway*, II. 277c
- , essential oil, II. 278a
- oil, carveol in, II. 101d
- , carvone in, II. 406b
- "*Carbacaine*," II. 280b
- Carbamic acid*, II. 278b
- Carbamide*, acetyl  $\alpha$ -bromo- $\alpha$ -ethylbutyryl-, I. 1c
- Carbarnino-acids*, I. 320d
- Carbaminoylcholine*, III. 91a
- Carba* process of  $\text{CO}_2$  production, II. 327b
- "*Carbasone*," I. 187a; II. 278b
- Carbazide*, II. 278b, 303c
- Carbazines*, I. 133d
- Carbazolimide*, II. 278b, 323a
- Carbazole*, II. 278c
- , N-acetyl-, II. 279b
- , -1-carboxylic acid, II. 279c
- , 3:6-diamino-, II. 280b
- , 3-diazonium hydrochloride, III. 595a
- dyes, I. 420d
- from brucine and strychnine, II. 278d
- in anthracene, detection, I. 387b
- indophenol, II. 280a
- , N-nitroso-, II. 279c
- , pigments from, II. 280b
- Carbazolene*, II. 279a
- Carbazones*, I. 133d
- Carbazyl ketones*, II. 280a
- Carbene*, I. 87a
- "*Carbest*," II. 682b
- Carbides* (see also Acetylene, metallic derivs.), II. 280b
- "*Carbitol*," II. 282a
- Carbocamphenilone*, II. 238b
- "*Carbocite* process," V. 365b
- Carbocyanines*, 2:2-, 2:1-, and 4:1-, III. 516c
- , indo-, indothua-, indoxa- and oxathua-, III. 523d
- , unsymmetrical, III. 523b
- "*Carbofrax*," II. 361a
- Carbohydrase*, definition, II. 282a
- Carbohydrases*, functions, IV. 314b
- Carbohydrates*, II. 282a
- "*Carbohydrates*, digestible," IV. 599d
- Carbohydrates* in feeding stuffs, IV. 592d, 603a
- rice, II. 494b
- starch, II. 482a
- cabbage, II. 183a
- Carbohydrates* in carrots, II. 403d
- "*Carbohydrates*, soluble," IV. 599d
- Carbohydrazide*, II. 303c
- Carbolic acid*, or phenol, II. 303c; III. 207d, 212c
- , liquid, III. 428b
- Carbolineum*, II. 308d; III. 421d
- Carbon*, II. 308d
- "*Carbon*," I. 3d
- Carbon*, activated, I. 140a
- Carbonado*, I. 3d; II. 309d, 356d; III. 575a
- "*Carbonalpha*," II. 313a
- "*Carbonate*," abrasive, I. 3d; II. 356d; III. 575a
- Carbonate*, detn., gravimetric, II. 591c
- "*Carbonate* of barytes," I. 651a
- Carbonates*, behaviour with indicators, II. 610b
- of sugars, II. 201b
- , qualitative reactions, II. 569d
- Carbon bromide*, II. 320c
- carbon oxides equilibrium, V. 368a
- chlorosulphides, from  $\text{CS}_2$ , II. 353c
- chromium alloy, III. 101d
- compounds, II. 320b
- , combustion analysis, II. 615c, micro, II. 630a
- , qualitative tests, II. 615a
- , detection, II. 568d
- dibromide, II. 320c
- dioxide, II. 323c
- , as fertiliser, II. 326b
- atmosphere for food storage, II. 326b; V. 293d
- , detn., gasometric, II. 677c, gravimetric, II. 682b, and volumetric, II. 612d, 615d, 682a
- , physical, methods, II. 682b
- fumigation, II. 361c; V. 394d
- , liquid, II. 326c, 328a
- , reaction with Grignard reagents, II. 363b
- , solid, II. 326c, 388c; IV. 56a
- disulphide, II. 328b
- , detection, II. 569a, 682d
- , detn., II. 682d
- , in fumigated food, V. 396c
- fumigation, II. 344a; V. 396b
- , luminescent oxidation, III. 23b
- , prepn. from hydrocarbons, II. 337d
- , reaction with chlorine, II. 353a
- , recovery, II. 338b
- , removal from benzole, I. 674d
- , specification, II. 344a
- vapour, absorption in oil, II. 340b
- fluorides, II. 323b
- fluorochlorides, II. 356a
- Carbonic anhydrase*, II. 356d
- Carbonisation*, see also Coal carbonisation.
- Carbonisation*, high temperature, V. 367b
- , low temperature, V. 364d
- of wool, II. 14b; IV. 123c
- Carbonite*, II. 357a
- "*Carbonite*," IV. 463d
- Carbon monosulphide*, II. 322b
- monoxide, II. 344b
- , action on metals, II. 357a
- and methanol, acetic acid from, II. 425c
- , blood test, II. 682d; VI. 106a
- , detection, II. 569a, 682b; III. 21b
- , detn., gasometric, II. 678c
- , high pressure reduction, II. 425c
- , reaction with hydrogen, VI. 378d
- oxysulphide, detection and detn., II. 683a
- , prepn., II. 338a
- "*Carbon papers*," VI. 490a
- Carbon* process in photography, III. 110a
- Carbons*, decolorising, II. 311d, 320a
- Carbon subnitride*, II. 321c
- suboxide, II. 351d
- , reacts as malonic anhydride, II. 352c
- subsulphide, II. 323c
- sulphidosemide, II. 323b
- tetrabromide, formation, II. 356a
- , prepn., II. 320b
- , presence in bromine, II. 118b
- tetrachloride, I. 105c; II. 353a
- fire extinguisher, V. 209c
- in fumigants, II. 344a
- warfare, III. 10c
- , prepn., III. 11a
- tetrafluoride, II. 323b, 350a
- tetraiodide, II. 321c
- tribromide, II. 320c
- Carbonyl-J-acid*, IV. 222d
- azide, II. 278b, 323a
- bromide, II. 323a
- chloride, see also Phosgene.
- , carbon tetrachloride from, II. 354d
- , prepn., II. 321c, 354d, 355c
- , properties, II. 321c
- compounds, detection and detn. as hydrazones, II. 626c; VI. 304c
- cyanide, II. 322b
- "*Carbonyling*" of nickel, II. 351a
- Carbonyl nitride*, II. 278b
- selenide, II. 323b
- Carbonyls*, metal, II. 351a, 357a
- Carbonyl sulphide*, II. 322c
- Carbo oven*, II. 311c
- Carboraffin*, II. 358d
- "*Carborundum*," abrasive, I. 3d, 4a
- flours, II. 359d
- occurrence, II. 280c
- production, II. 310d, 358d
- "*Carboxerin*," II. 361b
- "*Carboxide*," II. 361c; V. 395d
- "*Carboxide gas*," IV. 380b
- Carboxylase* in yeast, II. 99d; V. 10b

- Carboxyl group**, detn., II. 625d  
**Carboxylic acids**, II. 361c  
**Carboxypeptidase**, IV. 311d, 325b  
**Carbromal** or carbromalum, I. 141a  
**Carbo** process in photography, III. 111a  
**Carburetted water gas**, II. 345a; V. 469c, 490b  
 —, composition and cal. val., V. 472c  
 —, "gas oil," V. 472b  
 —, waste heat boiler, V. 471a  
**Carcinogenic hydrocarbons**, II. 378b  
**Carclazite** or carclazyte, II. 380b  
**Cardamoms**, II. 380b  
 —, essential oil, II. 381a  
**Cardboard**, casein adhesive in, II. 414b  
**Cardiac isoglycones**, II. 382b  
 — glycosides, II. 381a  
 "Cardiazol," II. 388c  
**Cardol**, I. 366a; II. 388c  
**Cardox** blasting process, IV. 502c  
 — cartridges, II. 388c  
**4<sup>o</sup>-Carene**, II. 388c  
**4<sup>o</sup>-Carene**, II. 389b  
**Carius** halogen detn., II. 620b  
 —, micro - method, II. 632a  
 — sulphur detn., II. 621c  
 —, micro - method, II. 632c  
**Carlic acid**, V. 52b  
**Carlosic acid**, V. 52b  
**Carminamide**, III. 220d  
**Carminazarin**, II. 390a  
**Carmino**,  $\alpha$ - and  $\beta$ -bromo-, III. 227a, b  
**Carminic acid**, II. 390a; III. 220d, 229d  
**Carminoisine**, II. 390a  
**Carnallite**, II. 109b, 195c, 212d, 390a  
**Carnauba** wax in candles, II. 204c  
**Carnaubic acid**, II. 390b  
**Carnaubyl alcohol**, II. 390b  
**Carnegine**, II. 390c  
**Carnelian**, II. 517b  
**Carnine**, II. 390d  
**Carnites**, II. 391a  
**Carnitine**, I. 387a; II. 391a  
**Carnose**, II. 391a  
**Carnosine**, II. 392a  
**Carnotite**, II. 392d  
**Carob tree**, II. 393b  
**Carol**, II. 393d  
**Carolic acid**, V. 52b  
**Carolinic acid**, V. 52b  
**Carone**, II. 393b  
**Caronic acids**, *cis*- and *trans*-, II. 389b, 393d  
**Caro's acid**, II. 393d; VI. 341a, 345b  
**Carotene**, II. 393d, 398d; III. 184d  
 —,  $\alpha$ - and  $\beta$ -, II. 397a, 394c  
 —, detn., colorimetric, II. 394b  
 — in flour and wheat, II. 81c, 505c  
 —, occurrence in plants, II. 183a, 272b, 404a  
 —, sources, II. 394a  
 **$\beta$ -Carotene**,  $\beta$ -carotene aldehyde, structure, II. 396b  
 —, conversion into vitamin A, II. 394d  
 —, dihydroxy-, II. 395b  
 **$\gamma$ -Carotene**, II. 397b  
**isoCarotene**, II. 394d, 397d  
**pseudo- $\alpha$ -Carotene**, II. 397d  
**Carotenoids**, II. 151a, 397d  
 —, animal, II. 401c  
 —, bacterial, II. 401d  
 —, biosynthesis, II. 401d  
 —, chromatographic separation, II. 398b  
 — in butter, II. 163b  
 —, physiological importance, II. 402a  
 —, plant, structure, II. 398a, 399a  
**Carotene**, II. 395b  
 **$\beta$ -Carotene**, II. 399b  
 — aldehyde, II. 395b  
 —, oxidation, II. 395b  
**Carot gum**, VI. 150c  
**Caroubin**, I. 660a; II. 393b, 403a  
**Caroubinose**, II. 393b, 403a  
**Carpaine**, II. 403a  
 —, nitroso-, II. 403b  
**Carpamic acid**, II. 403b  
 "Carphenol," II. 150b  
**Carpine**, II. 403c  
**Carpotroche** oil, II. 403c, 523b  
**Carrageen**, I. 190b; II. 403c  
 —, detn., II. 403d  
**Carrageenin**, II. 403d  
**Carrot**, II. 403d  
**Carthamidin**, II. 404b  
**Carthamin**, II. 404b  
**Carthamus tinctorius**, IV. 86b  
 "Cartox," V. 395d  
**Carum carvi**, II. 277c; IV. 1c  
 — *petroselinum*, I. 450c  
**Carvacrol**, *p*-amino-, I. 326a  
 —, chloro-, II. 404c  
 — from camphor, II. 212d  
 — — carvenone, II. 404d  
 — in camphor oil, II. 249c  
 —, reduction to carvomenthol, II. 405c  
**Carvasept**, II. 404c  
**d-Carvene** in caraway oil, II. 278a  
**Carvenene**, II. 404c  
**Carvenol**, II. 404d  
**Carvenone**, II. 404c; IV. 9b  
 — from camphor, II. 212d  
 —, reduction to carvomenthol, II. 405b  
**Carveol**, II. 404d  
 — from carvene, II. 407b  
 — in caraway oil, II. 278b  
 —, reduction to carvomenthol, II. 405c  
**Carvestrene**, II. 405a  
 — from carone, II. 393c  
**Carviolacin**, V. 55c  
**Carviolin**, V. 55c  
**Carvomenthol**, II. 405a  
 —, formation, II. 405a, 407b  
 —, oxidation, II. 406a  
**Carvomenthone**, II. 405d  
 — from carvene, II. 407b  
 — — carvotanacetone, II. 408c  
**Carvomenthylamines**, II. 406d  
**Carvone**, II. 406b; IV. 1c, 5a  
 —, hydroxy-, II. 408b  
 — in caraway oil, II. 278a  
 —, reduction, II. 404d, 405c, 407b
- Carvotanacetone**, II. 408a, 408b  
 —, reduction, II. 405c  
**Caryilamine**, II. 393c  
**Caryophyllene** in *Canella alba*, II. 269c  
**Caryophyllenes**, II. 408d; III. 183c  
**Caryophyllenic acid**, II. 409b  
*Caryota urens*, V. 168b  
**Casale** process, I. 336d  
**Casca bark**, IV. 335d  
**Cascalotte**, VI. 153b  
**Cascara sagrada**, II. 410c  
 — — substitute, I. 198a  
**Cascarilla**, essential oil, II. 411a  
**Cascarillic acid**, II. 411a  
**Cascarol**, II. 410d  
**Case**-hardening with sodium cyanide, III. 485b  
**Casein**, II. 411a  
 —, adhesives, I. 142d  
 —, as photographic film, II. 448a  
 — fibres, II. 416a; IV. 125c; V. 115c  
 — in curd, II. 163a  
**Caseinogen**, II. 411a  
**Casein** plastics, II. 416c  
 — wool, II. 416a  
**Cashew nut**, I. 12b, 365d  
 — — shell oil, I. 360a  
**Casimiroedine**, II. 417d  
**Casimiroine**, II. 417d  
**Casimiroitine**, II. 418a  
**Cassaidine**, IV. 336a  
**Cassaine**, IV. 336a  
**Cassava**, II. 418c  
**Cassel earth**, II. 418b  
**Cassia**, II. 418b; III. 182a  
*Cassia angustifolia*, III. 550c  
**Cassia**, essential oil, II. 418b  
*Cassia occidentalis*, III. 257b  
**Cassia oil**, cinnamaldehyde in, III. 180a  
*Cassia tora*, II. 419a  
**Cassie oil**, I. 11c  
**Cassiterite**, II. 419b  
**Castagnitol**, III. 27c  
**Castelagenin**, II. 119d  
**Castelin**, II. 419c  
*Castilleja elastica*, III. 546a  
**Castner** electrolytic cell, III. 55a  
**Castor oil**, II. 420a  
 — — in dopes for film manufacture, II. 448b  
 — — — lacquers, II. 468a  
 — — —, specification, II. 472c  
 — or castoreum, II. 419d  
 "Catadyn" process, IV. 24d  
**Catalase**, II. 422c; IV. 315b; VI. 168b, 346a  
 —, constitution, VI. 168c  
 — in bread 'rope,' II. 84b  
 — — mulling, II. 89a  
 — — rice, II. 495d  
 —, mol. wt., VI. 168b  
 —, prepn., VI. 168b  
 "Catalin," II. 422c  
 "Catalpo," II. 422d  
**Catalysts** (see also Catalyst(s); Chain reaction: Esterification, catalytic; Reactions, heterogeneous; and catalysed processes, as Hydrogenation), II. 422d  
 —, acid, relation to conductivity, VI. 242a

- Catalysis**, active centres in, II. 540c  
 —, activity coefficients in, VI. 244a, 246a  
 —, adsorption in, II. 539c; VI. 215a, 314c  
 — and dissociation theory, VI. 241d  
 — by metallic halides, VI. 259a  
 — — ions, VI. 258d  
 —, catalytic constant in, VI. 241a  
 —, definition, VI. 255c  
 —, dual theory, VI. 249c  
 —, general acid-base, VI. 249b  
 —, homogeneous (*see also* Catalysis), VI. 240c  
 —, hydrogen ion in, VI. 253c  
 —, hydroxyl ion in, VI. 253c  
 —, inhibition (*see also* Catalyst poisons), VI. 260c  
 — in industrial chemistry, II. 422d  
 — — inert solvents, VI. 251b  
 — — non-aqueous solvents, VI. 244b, 251a, 255b  
 —, mass action in, II. 539c  
 —, negative, *see* Catalysis, inhibition; Catalyst poisons.  
 — of pinene isomerisation, II. 258b  
 —, primary salt effect in, VI. 240b  
 —, reaction velocity in homogeneous, VI. 241a  
 —, secondary salt effect in, VI. 244b  
 —, spontaneous reaction in, VI. 251a  
 —, statistical effect in, VI. 253a  
 —, strong electrolytes in, VI. 243d  
 —, theories, VI. 372c  
 —, water molecule in, VI. 253c  
**Catalyst(s)**, *see also* Antioxidants; Auxin; Catalysis; Enzymes; Hormones; Hydrolysis; and under catalysed processes.  
**Catalyst poisons** (*see also* Anticatalysts; Catalysis, inhibition; Catalysts, nickel, poisons), I. 331a; II. 423c, 540c; VI. 211c, 218a, 260c, 336d  
**Catalysts**, prepn., *see* Hydrogenation; II. analysis; H. of coal.  
 —, promoter actions, IV. 316a, 355c  
 — structure, VI. 377c  
 —, typical, VI. 212d  
 —, uniformity, VI. 380b  
**Catalysts**, action on water gas, II. 349b  
 —, dehydrating, IV. 350c  
 —, "foraminated," VI. 181d  
 —, massive and colloidal, VI. 216c  
 —, nickel, poisons, VI. 180c, 181b  
 — of oil hydrogenation, II. 427a; VI. 178b  
**Catalytic** esterification, IV. 338d  
 — oxidation of aldehydes, VI. 261b  
 — — sulphites, VI. 260d  
 — power and acid-base strength, VI. 252d  
**Cataphoresis**, III. 283c  
**Catapleiite**, II. 429c  
**Catechin**, II. 433d, 435c  
 "Catechin C," II. 435c  
**dl-Catechin**, I. 11b  
**Catechol**, II. 429c  
 — and acyl and aryl derivs. in pharmacy, II. 431a, 432b  
 — as bactericide, II. 431a  
**Catecholcitraconein**, II. 433b  
**Catechol esters**, II. 431b  
 —, rearrangement, II. 432a  
**Catecholitaconein**, II. 433b  
**Catechololphthalein**, II. 433b  
**Catechol**, rare earth derivs., II. 515d  
**Catechols**, alkyl, as disinfectants, II. 432b  
**Catechol sulphonic acids**, II. 432d  
 — tannin in heather, II. 235a  
**Catechu**, II. 433b; IV. 126b  
**Catechutannic acid**, II. 138b  
**Catellagic acid**, II. 439a  
**Catenarin**, V. 55a  
**Catha edulis**, I. 11b; IV. 317b  
**Catharometer**, V. 300d  
**Cathartin**, II. 439a  
**Cathartogenic acid**, II. 439a  
**Cathidine**, I. 11b; II. 439b  
**Cathine**, I. 11b; II. 439b; IV. 317b  
**Cathinine**, I. 11b; II. 439b  
**Cathode efficiency**, IV. 201c  
**Cathodic protection of metals**, III. 392c  
**Cation acids**, VI. 247b  
**Cat's-eye**, oriental, III. 119a  
**Cauliflower**, II. 182b  
**Caulophylline**, II. 439b  
**Cây** (Cây lat, Cáy-cáy lat, II. 439b; IV. 1a  
**Cayenne pepper**, II. 273b  
**C.C.** (earthenware), VI. 8d  
**C.E.** (explosive), IV. 485a  
**Cedar camphor**, II. 439c, 411a  
**Cedarite**, I. 302c  
 "Cedar, Moulmeu," II. 439d  
**Cedar nut oil**, IV. 80a  
**Cedarwood**, essential oil, II. 439c  
**Cedra-Cedrat**, II. 439c  
**Cedrat oil**, III. 190d  
**Cedrela toona**, II. 439d  
**Cedrene**, II. 439c, 440c, 411a  
**Cedrenol**, II. 439c  
**Cedriret**, II. 440d  
**Cedrol**, II. 439c, 441a  
 —, dehydration, II. 440c  
**pseudoCedrol**, II. 139c, 411a  
**Cedrone**, II. 440c  
**Cedrus atlantica**, I. 533c  
**Ceiba pentandra**, V. 108c  
**Celadonite**, VI. 136a  
 "Celanese," I. 39c  
 "Celastoid," II. 480a  
 "Celatene," I. 41b, 205c  
 "Celcot," IV. 231a  
**Celery cabbage**, II. 182b  
 —, celeriac, II. 441b  
 —, essential oil, II. 441c, 442a  
 — seeds, II. 441d  
**Celestine or celestite**, II. 442b  
**Celite**, II. 141b, 228b  
 "Cellastine," II. 480a  
**Celliamine** (cellamin), II. 442c; VI. 200b  
 "Celliton dyes," I. 41a  
**Celliton Rubine B**, I. 41b  
**Cellobiase**, II. 442c  
**Cellulose**, II. 208b, 442c  
 —, relation to cellulose, II. 457a  
 — units in cellulose, II. 301c  
**Cellodextrins**, II. 442d  
**Cellulohexose**, II. 302a, 412d  
 "Cellomold," II. 480a  
 "Cellophane," II. 442d, 452b, c  
 "Cellosolve," II. 443a; IV. 378c  
**Cellotetrose**, II. 290a, 302a, 442d  
**Cellotriose**, II. 299a, II. 302a, 412d  
**Cellotropin**, II. 443b  
**Cellulase**, II. 443b  
**Celluloid**, II. 443b  
 — camphor in, II. 249c, 260a  
 — plastics, II. 446a  
 — production, II. 461b  
**Cellulose** (*see also* Cellulose fibres), II. 282a, 456d  
 — acetate, chain length, II. 301d  
 — — in photographic films, II. 417a  
 — — production, II. 447b, 461d; V. 121d  
 — — rayon dyes (*see also* Acetate silk dyes; Dyeing; Azo-dyes), I. 205c  
 — — spinning, V. 123b  
 — — ripening, "V. 123a  
 acetates, acetone-soluble, II. 161d; V. 122b  
 —, chloroform-soluble, II. 461d  
 —, blending, II. 3c  
 —, bran, II. 59a  
 —, cotton, properties, II. 4b  
 —, cuprammonium, II. 463b; III. 355a; V. 113a, 116a  
 — dispersions, II. 450d  
 —, esparto, xylan in, II. 303c  
 — esters in photographic film, II. 417a, 448a  
 — ester solutions, II. 467d; III. 395b  
 — ethers in photographic films, II. 418a  
 — fibres (*see also* Fibres, artificial, or rayon; Fibres, cotton; Fibres, vegetable), II. 465b  
 — in dyeing, *see* Dyeing; Azo-dyes.  
 — finishes, butanol in, II. 169c  
 —, formula, II. 301c, 457c  
 —, hydration, II. 450c  
 —, hydrolysis, II. 443b  
 — in feeding stuffs, IV. 593a  
 — lacquers, II. 467d; III. 395b  
 — nitrate, *see also* Celluloid; Celluloid plastics; Cellulose; Cellulose lacquers; Explosives; Fibres, artificial, or rayon.  
 — for films, II. 447a  
 — nitrates, IV. 501c  
 — nitrate silk, V. 114d  
 —, nitration, II. 443c  
 —, nitro-, *see* Cellulose nitrate.  
 — nitroacetate, films, II. 447d  
 — plastics, II. 474b  
 — polymerisation, V. 129a  
 —, regenerated, azo dyes for, IV. 234a  
 —, viscosity of cuprammonium, II. 468b  
 — xanthate or xanthogenate, II. 442d, 465b; V. 118a

- Celtis occidentalis*, IV. 278*d*  
**Celtium**, II. 480*b*  
**Cement** (*see also* Portland cement), II. 129*b*, 135*c*  
 —, aluminous, II. 146*b*  
 —, casein, II. 414*b*  
 —, celluloid, II. 445*d*  
 —, cold process slag, II. 145*a*  
 —, lime, natural, II. 133*d*  
**Cementite**, II. 280*d*, 480*c*  
**Cement**, magnesium oxy-chloride, II. 135*c*  
**Cements**, chalk in, II. 518*c*  
**Centaurea**, II. 480*c*  
**Centaur**, II. 480*c*  
 "Centralites," stabilisers, II. 480*c*; IV. 521*a*  
 —, detn., IV. 533*b*  
**Centrifugal** pot for rayon, V. 117*a*, 120*d*  
**Cephaeline**, II. 480*d*; IV. 281*a*  
**Cephalanthin**, II. 481*a*  
**Cephalin**, *see* Kephalin.  
**Cepharanthine**, II. 481*a*  
**Ceradia**, II. 481*b*  
*Cera ficu*, V. 171*a*  
 "Ceralumin," I. 253*a*  
*Ceranium rubrum*, I. 200*b*  
**Cerargyrite**, II. 481*b*  
**Cerasin**, II. 481*d*  
**Ceratonia** gum, *C. siliqua*, I. 201*b*, 658*d*; VI. 156*c*  
**Cerberetin**, II. 481*d*  
**Cerberin**, II. 387*c*, 481*d*  
**Cereals**, II. 481*d*  
**Cerebron**, II. 506*c*; VI. 93*c*  
**Cerebrose**, II. 506*c*  
**Cerebrosides**, II. 506*c*  
**Cerite**, II. 512*a*  
**Ceresin**, II. 204*c*, 506*d*  
**Cerfluorite**, II. 506*d*  
**Ceria**, II. 510*a*  
**Ceric carbide**, II. 509*d*  
 — chloride, organic compounds, II. 510*b*  
 — hydroxide, II. 510*b*  
 — nitrate, II. 510*d*  
 — oxide, II. 510*a*  
 —, catalyst for oxidation of carbon monoxide, II. 317*a*, 351*d*  
 — selenate, II. 510*c*  
 — sulphate in analysis, II. 510*b*, 647*d*; VI. 441*c*  
**Cerin**, II. 507*a*  
**Cerine**, II. 512*a*  
**Cerinstein**, II. 512*b*  
**Cerite**, II. 507*a*, 511*b*, 512*b*  
**Cerium** (*see also under* Ceric, Cerous), II. 507*a*  
 — azide, II. 509*b*  
 —, detn., potentiometric, I. 707*b*  
 —, —, volumetric, II. 655*b*  
 — hydride, II. 508*c*  
 — in photography, II. 511*a*  
 — metals and earths, II. 511*b*  
 — nitride, II. 509*b*  
 — peroxide, II. 510*d*  
 — phosphate, mineral, III. 120*a*  
 —, qualitative reactions, II. 555*b*, 562*b*, 568*c*  
 —, separation from rare earths, II. 507*d*, 568*d*  
 — silicate, II. 507*a*  
 — silicide, II. 507*c*  
**Cerosig**, II. 516*b*  
**Cerosiline**, II. 516*b*  
**Cerotene**, II. 516*b*  
**Cerotic acid**, II. 516*c*  
 — in arachis oil, I. 456*a*  
**Cerotic acid** in beeswax, II. 507*a*  
 — — brussels sprouts, II. 119*c*  
 — in rice, II. 494*b*  
**Cerotin**, II. 516*c*  
**Cerous acetylacetonate**, II. 509*d*  
 — bromate, II. 508*d*  
 — carbonate, II. 509*c*  
 — chloride, II. 508*d*  
 — cobalticyanide, II. 509*c*  
 — dimethylphosphate, II. 509*d*  
 — fluoride, II. 508*d*  
 — halides, II. 508*d*  
 — hydroxide, II. 509*a*  
 — iodate, II. 508*d*  
 — nitrate, II. 509*b*  
 — oxalate, II. 509*c*  
 — phenoxide, II. 509*c*  
 — sulphate, II. 509*b*  
 — sulphide, II. 509*a*  
 — tungstate, II. 509*c*  
**Cerulignol**, I. 661*b*  
**Cerussite**, II. 516*d*  
**Cervantite**, I. 410*a*  
**Ceryl alcohol**, II. 119*c*, 390*c*, 516*c*  
 — cerotate, II. 516*c*  
 "Cettacol," II. 516*d*  
**Cétine**, II. 516*d*  
**Cetoleic acid**, III. 247*b*  
 "Cetosol," II. 516*d*  
**Cetyl alcohol**, II. 517*a*  
 — *d*-glucoside, VI. 86*c*  
**Cetylmalonic acid**, II. 517*a*  
**Cetyl palmitate**, II. 516*d*  
**Cevadilline**, II. 517*a*  
**Cevadine**, II. 517*a*  
**Ceylon oil**, III. 239*c*  
**Ceyssatite**, III. 579*d*  
**C** function of combustion, V. 246*c*  
**Chabazite**, I. 150*d*  
*Chaillitia toxicaria*, II. 517*a*  
**Chain reactions**, II. 533*c*; IV. 83*a*, 418*a*; VI. 260*d*  
**Chairamidine**, II. 517*a*; III. 128*a*, 151*d*  
**Chairamine**, II. 517*a*; III. 128*a*, 151*d*  
**Chalcantithe**, II. 517*a*; III. 341*c*, 357*b*  
**Chalcedonite**, II. 517*b*  
**Chalcedony**, II. 25*a*, 517*a*  
**Chalcocite**, II. 517*c*; III. 341*c*, 355*a*  
**Chalcopyrite**, II. 32*d*, 517*c*; III. 341*c*  
**Chalcosine** (*see also* Chalco-cite), II. 517*c*  
**Chalcostibite**, II. 518*a*  
**Chalcotrichite**, II. 518*a*; III. 451*a*  
**Chalk**, II. 220*a*, 518*a*  
 — fertiliser, V. 74*a*  
 —, French, II. 518*c*  
 — chalkone group, II. 518*c*  
**Chalmersite**, III. 455*a*  
**Chalybite**, II. 519*c*  
**Chamazulene**, I. 119*d*, 381*a*; II. 520*a*  
**Chamber process** sulphuric acid, II. 423*b*  
**Chamoising** process, III. 551*b*  
**Chamomile**, essential oil, I. 119*d*, 381*a*; II. 520*a*  
 — flowers, II. 520*a*  
**Chamomillol**, II. 520*b*  
**Chamosite**, II. 520*b*  
**Chamotte**, II. 520*b*  
**Champacol**, VI. 142*c*  
**Channa**, II. 520*c*  
**Ch'an su**, II. 388*b*  
**Chapman's** formula for explosion wave velocity, IV. 438*c*  
**Charcoal**, II. 309*a*, 310*c*, 311*c*  
 — activation, II. 333*c*  
 — active, II. 315*c*  
 —, —, from bran, II. 62*d*  
 —, adsorption of carbon disulphide on, II. 340*b*  
 —, animal, II. 311*c*  
 —, catalysis by, II. 428*d*  
 — for gunpowder, IV. 455*d*  
 — in respirators, II. 19*b*  
 —, Meiler, II. 310*d*  
 —, peat, V. 360*a*  
 —, retentivity, II. 318*a*  
 —, Urban, II. 317*a*  
 —, wood, II. 310*c*; V. 359*d*  
**Chard**, II. 520*c*  
**Chardonnet** process, II. 471*d*; V. 113*a*  
**Charles's** law, VI. 412*a*  
**Chartreuse**, II. 520*c*  
**Chasing**, V. 188*c*  
**Chasmantherin**, II. 235*b*  
**Chatterton's** compound, VI. 159*b*  
**Chaulmoogra** (*Chaulmugra*), oil group, II. 521*b*  
**Chaulmoogric acid**, II. 521*b*, 523*c*  
**Chavibetol**, I. 687*c*  
**Chavicin**, II. 523*c*  
**Chay-aver**, *see* Chay root.  
**Chayote**, II. 524*d*  
**Chay root**, II. 523*c*  
**Chebulinic acid**, VI. 86*d*  
**Cheddaring** of cheese, II. 527*a*  
 — of rennet, II. 413*a*  
**Cheddites**, II. 525*a*; IV. 465*b*  
**Chessa** sticks, II. 525*d*  
**Cheese**, II. 525*d*  
 "Cheese," cider pomace, III. 124*d*  
**Cheese** ripening, II. 526*d*; V. 59*d*  
**Cheiranthin**, II. 387*d*, 527*d*  
*Cheiranthus cheiri*, I. 499*b*; II. 527*c*  
**Cheirinin**, II. 527*d*  
**Cheirolin**, II. 527*c*  
**Chelkiang**, V. 330*a*  
**Chelate** groups, III. 328*c*  
**Chelerythrine**, II. 528*d*  
**Chelidonine**, II. 527*d*, 528*b*  
*Chelidonium majus*, alkaloids, II. 527*d*  
 —, —, berberine from, I. 620*b*  
**Chellak**, II. 520*d*  
**Chellol**, II. 529*d*  
 — glucoside, II. 529*d*; VI. 86*d*  
**Chemawinite**, I. 302*c*  
**Chemical** affinity, II. 530*a*  
 "Chemical thermometer," V. 241*c*  
**Chemical warfare**, III. 7*b*  
 — defence, III. 18*a*  
**Chemick** in cotton bleaching, II. 3*d*  
**Chemicking**, II. 6*a*  
 — plant, II. 8*a*  
**Chemiluminescence**, III. 22*d*  
**Chemisorption** in ammonia synthesis, VI. 207*d*  
 — in catalysis, II. 422*d*; VI. 378*b*, 380*c*  
 — on charcoal, VI. 214*b*

- Chenodeoxycholic acid**, I. 680b  
**Chenopodium ambrosioides**, I. 501a; III. 24c  
**Chenopodium**, essential oil, III. 24c  
**Cherimoya**, III. 24d  
**Cherry**, III. 25a  
 — kernel oil, III. 25c  
 — - Laurel, essential oil, III. 26a  
 — - - leaves, III. 26a  
 " **Cherry pie**," VI. 191b  
**Chert**, III. 26a  
**Chessylite**, I. 583d; II. 25c; III. 26c  
**Chesting**, V. 188c  
**Chestnut**, III. 26d  
 extract, III. 27b  
**Chevreul's salt**, and solution, IV. 263b  
**Chian** turpentine, III. 28b  
**Chia seed oil**, IV. 86b  
**Chialtolite**, I. 370b  
**Chicago acid**, IV. 217a  
**Chick pea**, III. 29b  
**Chicle**, I. 120a; III. 30b  
**Chicory**, III. 30b, 256a  
**Chile saltpetre**, II. 231b; III. 31c  
 " **Chili nitre** " for glassmaking, V. 560c  
**Chillies**, II. 273b  
 " **Chilling** " of collodion, II. 408d  
**China clay**, III. 195d  
 — in plastics, II. 176b  
 — grass, III. 31b  
**Chinaphenin**, III. 33a  
**China-stone**, III. 32b  
 — - - - , mild purple, III. 32c  
 — wood oil, I. 198b; III. 33a; IV. 82c  
 — - - - , hydrogenation, VI. 185b  
 — - - - , prepn. for varnishes, IV. 80b  
 " **Chineonal**," III. 33a  
**Chinese cabbage**, II. 182b  
 — vegetable tallow, III. 33a  
 " **Chnitofo**," III. 33d  
 " **Chinoform**," III. 33d  
 " **Chinosol**," III. 33d  
 " **Chinotropin**," III. 33d  
**Chinovin**, sugars, II. 287c  
**Chinovose**, II. 287c; IV. 321a  
**Chinquapins**, III. 26d  
**Chiolite**, I. 261c, 286b; III. 33d  
**Chios** turpentine resin, III. 34a  
**Churata**, B.P., Churatin, III. 34a  
**Chiretta**, III. 34a  
**Chitenine**, III. 34a  
**Chitin**, III. 34a; IV. 311b; VI. 21c  
**Chitinase**, III. 34b; IV. 311b  
**Chitobiose**, III. 34b  
**Chitodextrin**, III. 34b  
**Chitosamine**, III. 34c  
**Chitotriose**, III. 34b  
**Chives**, III. 34c  
**Chloanthite**, I. 460a; III. 34d, 214b  
**Chloral**, III. 34d  
**Chloralamide**, III. 35c, 36a  
**Chloral hydrate**, I. 195b  
**Chloralose**, III. 35c  
**Chloramin**, chloramine-T, I. 140a; III. 36a  
**Chloranil**, III. 36b  
**Chlorargyrite**, II. 481c  
**Chlorates**, III. 66b  
 — , detn., gravimetric, II. 609d  
 — , qualitative reactions, II. 570d  
**Chlorazene**, III. 36b  
 " **Chlorbutol**," I. 70c, 371c; III. 36c  
**Chlorene**, I. 80a; III. 36b  
 " **Chloreton**," I. 70c, 371c; III. 36c  
**Chlorhydric ether**, IV. 358b  
**Chloride**, bromide and iodide, qualitative separation (see also Halogens), II. 565a  
 — of lime (see also Bleaching powder; Disinfectants), III. 60a  
**Chlorides**, qualitative reactions, II. 576b  
**Chlorination**, Deacon's reaction in, II. 351c  
**Chlorin-e**, III. 82b  
**Chlorine** (see also Halides; Halogens), III. 36c  
 as trace element, I. 505d  
 , bromine and iodine, sepn. and detn., II. 608a, 659c  
 , detection of gaseous, II. 576b, 683a  
 , detn., gravimetric, II. 606d  
 , — in hydrogenation analysis, VI. 362b  
 , — of gaseous, II. 683a  
 — , volumetric, II. 657c  
 ethoxide, IV. 363d  
 in flour, II. 81a  
 warfare, III. 9a  
 — , reaction with carbon disulphide, II. 353a  
 — - - - - monoxide, II. 350d  
**Chlorisol**, III. 77b  
**Chlorite** and hypochlorite, detn., volumetric, II. 609d  
 — , mineral, III. 571b  
**Chlorites**, qualitative reactions, II. 576c  
**Chloroazide**, I. 581b  
 " **Chlorocalcite**," I. 585d  
**Chlorocruorin**, III. 77b; VI. 168c  
 — in worms, II. 20a  
**Chloroform**, III. 77b  
 — , anæsthetic, I. 367c  
**Chloroformaldoxime**, V. 383b  
**Chloroform**, chemiluminescent reaction with hydrogen, III. 23b  
**Chlorogenic acid**, II. 196d, 198b, III. 79c, 251d  
**Chlorogenine**, I. 263c  
**Chlorophyceæ**, pigments, I. 200d  
**Chlorophyll**, III. 80a  
**Chlorophyllase**, III. 81c, 85a; VI. 398b  
**Chlorophyll** derivs. in mineral oils, VI. 165a  
**Chlorophyllides**, III. 81c  
**isoChlorophyllin-a**, III. 82b  
**Chlorophyll**, Mohs test, III. 84d  
 — , relation to blood pigments, II. 20c  
**Chloropicrin**, III. 11a, 85b  
 — fumigation, V. 397b  
 — in warfare, III. 8b, 10c, 13b  
**Chloroprene**, history, I. 74b, 87c  
 — production, I. 89a; II. 155d  
 — polymer, II. 153d; IV. 93c  
**Chloroquinol**, III. 86a  
**Chlororubine** in chay root, II. 523d  
**Chlorosis** of rice, II. 502a  
**Chlorosulphonic acid** in warfare, III. 11a  
 — , prepn., II. 350a  
 " **Chloroxyl**," III. 85a  
**Chloroxylinone**, III. 85a  
 " **Chlorylan**," III. 86a  
 " **Chochitzapoti**," II. 417d  
**Chocolate**, III. 86a  
 — fats, III. 88b  
**Chocolite**, V. 430a  
**Choke-damp** (after-damp), II. 323d, 341c  
**Cholam**, II. 482c  
**Cholanic acid**, III. 90b  
 — , tetrahydroxy-, I. 690a  
**alloCholanic acid**, II. 383a  
**Cholanthrene**, carcinogenic activity, II. 380a  
**Cholelyse**, III. 88d  
**Cholestandione**, III. 90c  
**pseudoCholestane**, III. 91c  
**Cholestanedione**, III. 89d, 90c  
**Cholesterol**, III. 89b  
**Cholestanonediol**, III. 89d  
**Cholestananol**, III. 89d, 90c  
**Cholestantriol**, III. 89d  
**Cholestene**, III. 91b  
**Cholestenone**, III. 89d, 90a  
**Cholesterilene sulphonic acid**, II. 203a  
**Cholesterol**, I. 690a; II. 201d; III. 88d  
 deficit in pellagra, II. 148b  
 — - - - - derivs., altered nomenclature, III. 91c  
 in raw wool, II. 12c  
 — , ring structure, II. 90b  
 — , structure of side chain, III. 90a  
**alloCholesterol**, III. 91c  
**isoCholesterol**, III. 92c  
 in raw wool, II. 12c  
**Cholesterophan**, III. 92d  
**Cholic acid**, I. 689b  
 — - - - - , dehydrogenation, III. 90d  
 — - - - - in cancers, III. 380a  
**Choline**, acetyl-, III. 93c  
 — - - - - , bromide, I. 73b  
 — - - - - , chloride, I. 73b  
 — - - - - , hydrolysis, II. 200b  
 — - - - - in ergot, IV. 331d  
 — and related substances, III. 92d  
 — - - - - esterase, III. 93d, 94b  
 — - - - - , inhibition of, II. 200b  
 — in cabbage, II. 182d  
 — - - - - *Dictamnus albus*, III. 602c  
**Cholum**, II. 182c  
**Chondodendrine** (chondrodendrine), III. 94d  
**Chondodrine** (chondrodrene), III. 94d  
**Chondrin**, III. 94c; V. 509d; VI. 25d  
*Chondrodendron tomentosum*, III. 459d  
**Chondroitin**, III. 94d  
**Chondrosamine**, III. 94d  
*Chondrus crispus*, I. 199b; II. 403c  
**Chopin** extensimeter, II. 78b  
**Chopping nut**, II. 198d  
 " **Chorogi**," I. 497a  
**Chromammonium** compounds, III. 114b

- Chromanone**, 3-homoveratryl-7-methoxy-, II. 71d  
**Chromate**, detn., *see* Chromium, detn.  
**Chromates and dichromates**, III. 110b  
 —, qualitative reactions, II. 564c, 575c, 580b; IV. 173b  
 —, production, III. 103a  
**Chromatographic analysis**, II. 628a  
 — of carotenoids, II. 398b; III. 80d  
 — — dyes, IV. 174c  
**Chrome alum**, III. 100d  
 — ammonit explosive, IV. 554d  
 — iron-ore, III. 94d  
 — spinel, I. 264c  
 — steel, III. 105c  
**Chromic acid**, III. 101d  
 —, detn. and reactions, *see* under Chromates; Chromium.  
 —, electrolysis, III. 97b  
 —, electrolytic regeneration from chromium salts, II. 256d  
 — anhydride, *see* Chromic acid.  
 — hydroxide, III. 108b  
 — salts, *see* under Chromium.  
**Chroming**, definition, IV. 128c  
**Chromite**, III. 94d, 96b  
**Chromium** (*see also* under Chrome; Chromic; Chromous; Chromyl), III. 96a  
 —, active and passive, III. 98c  
 — alloys, III. 103d  
 — aluminium alloys, III. 103d  
 — and aluminium, analytical separation, VI. 299b  
 — as trace element, I. 505d  
 — azide, III. 109d  
 — borides, II. 44c; III. 110b  
 — carbide, II. 281a; III. 104d  
 — carbon alloys, III. 104d  
 — carbonyls, II. 357b; III. 90d  
 — chlorate, III. 101c  
 — chloride and Grignard reagent, II. 357c; III. 90d  
 — — its hydrates, III. 108c  
 — chromate, III. 101d  
 — cobalt alloys, III. 104c, 217a  
 — copper alloys, III. 104c  
 —, detn., assay, I. 522d  
 —, by electrodeposition or electrolysis, II. 701a  
 —, colorimetric, II. 670d  
 —, gravimetric, II. 605a  
 —, in chrome steel, II. 655d  
 —, potentiometric, II. 708a  
 —, volumetric, II. 655c  
 —, —, Mn present, II. 662c  
 — dioxide, III. 101d  
 —, drop reaction, II. 580b; III. 96c  
 —, electrodeposition, IV. 267b  
 — fluoride, III. 109c  
 — hydride, III. 99d  
 — iron alloys, III. 105b  
 — lakes in dyeing, IV. 141b  
 — molybdenum alloy, III. 104d  
 — nickel alloy, III. 104b  
 — nitrate, III. 110a  
 — nitrate, III. 109c  
 — oxalates, III. 115b  
 — oxide, III. 106b  
 — phosphate, III. 100a  
 — platinum alloy, III. 104a  
**Chromium**, qualitative reactions (*see also* Chromates), II. 552a, 575b  
 —, —, rare metals present, II. 554a, 556d  
 — silicofluoride, III. 109c  
 — steel, *see* Chrome steel.  
 — sulphate and its hydrates, III. 100b  
 — zinc alloy, III. 103d  
 — — oxide catalyst in methanol production, II. 350a, 425c  
 — — — paraffin production, II. 350b  
**Chromiform**, III. 115c  
**Chromogen**, III. 308c  
**Chromone**, III. 115c  
**Chromophores**, III. 308b  
**Chromosphere**, VI. 300b  
**Chromotropes**, III. 115d  
**Chromotropic acid**, III. 115d; IV. 205d  
**Chromous bromide**, III. 109b  
 — chloride, III. 107d  
 — iodide, III. 109b  
 — oxide, III. 106b  
**Chromyl chloride or chromyl dichloride**, III. 102c, 109a  
**Chrysamine**, I. 131a, 133a  
**Chrysanthemin**, III. 115d; IV. 260a  
**Chrysarobin**, III. 116b  
 —, triacetyl-, IV. 402a  
**Chrysotropic acid**, III. 117d  
**Chrysazin**, I. 212d, 222b  
 —, diamino-, I. 205c  
 — 2:7-disulphonic acid and Na salt, I. 390b, 392d  
 —, hydroxy-, I. 212d, 225d  
**Chrysazines**, dihydroxy-, I. 227a  
**Chrysazin**, 2:4:5:7-tetranitro-, I. 228b  
 — 2:4:5:7-tetrasulphonic acid, I. 390b  
**Chrysene**, III. 118a  
**Chrysin**, III. 118d; VI. 97b  
**Chrysoberyl**, I. 261c, 685a; III. 119a; VI. 13c  
**Chrysocolla**, III. 119b, 341c, 355d  
**Chrysoeriol**, IV. 333d, 331b  
**Chrysogen**, I. 384d, 385a; III. 119c  
**Chrysogenin**, V. 54d  
**Chrysolite**, III. 119d  
**Chrysonaphthazine**, I. 568a  
**Chrysophanic acid**, I. 433a; III. 116c  
 — in *Cascara sagrada*, II. 410d  
**Chrysophanol**, III. 116c  
**Chrysoprase**, II. 517c  
**Chrysoquinone**, III. 118d  
**Chrysotile**, I. 499d  
**Chrysotoluazine**, I. 568a  
**Chufa**, III. 119d  
**Churchite**, III. 120a  
 — "Churi butter," I. 654a  
**Chymase**, III. 120a  
**Chyme**, I. 690b  
**Chymotrypsin**, III. 120a; IV. 311d  
**Ciba** electrolytic cell, II. 54b, 57c  
 — "Cibacet" dyes, I. 42a  
 — "Cibanone" dyes, III. 120b  
**Cichorigenin**, III. 120b  
**Cichorin**, III. 120b  
**Cichorin**, III. 413a  
**Cichorium endivia**, IV. 308a  
 — *intybus*, III. 30b  
**Cicutoxin**, III. 120b  
**Cider**, III. 120c  
 —, blackening, III. 127b  
 — sickness, III. 127a  
**C.I.E.**, colorimetric standards, III. 289c, 301a  
 — "Cignolin," I. 433a; III. 117c, 120c, 127d  
**Cimicifuga racemosa**, I. 137a  
 — "Cincaine," III. 127d  
**Cinchamidine**, III. 128a, 152a, 162b  
**Cinchene**, III. 138b, 158c  
**Cincholoipon**, III. 140b, 164c  
*homoCincholoipon*, synthesis, III. 144c  
 — ester, N-benzoyl-, III. 146a  
**Cincholoiponic acid**, III. 138a, 140b, 141c, 159d  
**Cinchomeronic acid**, III. 127d  
**Cinchona alkaloids**, III. 127d  
 —, extraction and estimation, III. 130a, 131b  
 —, structural formulae, III. 137c  
 —, totaquina detn., B.P. method, III. 132b  
 —, —, Committee method, III. 133a  
 — bark, analyses and methods, III. 129a, 131b  
 —, history, III. 127d  
 —, variety, II. 234b  
 — "Cinchona febrifuge," III. 169a  
**Cinchonamine**, III. 128a, 152a  
**Cinchona**, Senegal, II. 108b  
**Cinchonhydriene**,  $\alpha$ - and  $\beta$ -, III. 157c  
**Cinchonicine**, *see* Cinchotoxine.  
 $\alpha$ -iso- $\beta$ -Cinchonicine, III. 156c  
**Cinchonidine**, acetyl-, III. 153b  
**Cinchonidine** and quinine tartrates, polarimetry, III. 133c  
 —, derivs. and salts, III. 152b  
 —, reaction with mineral acids, III. 150a  
 —, separation from quinine, III. 131b  
 $\beta$ - or  $\gamma$ -Cinchonidine, III. 153c  
*apoCinchonidine*, III. 153c  
*isoCinchonidine*, III. 153c  
**Cinchonigine**, III. 156d  
**Cinchonilene**, III. 156b  
**Cinchoninal**, III. 140a, 158d  
**Cinchonine**, III. 128a, 154b  
 —, acetyl-, III. 155d  
 —, benzoyl-, III. 155d  
 —, reaction with mineral acids, III. 150a  
 —, structural formula, III. 142a  
*alloCinchonine*, III. 157a  
 $\alpha$ -isoCinchonine, III. 156b  
 $\beta$ -isoCinchonine, III. 156c  
 $\delta$ -Cinchonine, III. 157c  
*pseudoCinchonine*, III. 157a  
**Cinchoninic acid**, III. 138a, 141c, 159a  
 — "Cinchonino," III. 127d, 172b  
**Cinchoninone**, III. 138b, 158a, 162b  
**Cinchophen** (*see also* "Atophan"), I. 539c; III. 85b, 178d



- Cinchotomidine**, III. 139*d*, 154*b*  
 — from cinchonidine, III. 152*d*  
**Cinchotennine**, III. 139*d*, 159*a*  
**Cinchoticine**, III. 163*c*  
**Cinchotine**, III. 162*d*  
**Cinchotinotoxine**, III. 163*c*  
**Cinchotoxine**, III. 128*a*, 142*d*, 157*d*  
 **$\alpha$ -Cinemic acid**, III. 170*c*  
**Cineole** from cajuputol, II. 198*c*  
**Cineole** in cardamoms, II. 381*a*  
 — essential oils, II. 249*b*, 269*c*; III. 179*b*, 198*d*  
 — from *Eucalyptus* spp., II. 25*b*; IV. 390*b*  
**1:4-Cineole**, III. 179*a*  
**1:8-Cineole**, III. 179*b*  
**Cineolic acid**, III. 179*b*  
**Cinnabar**, III. 179*d*  
 —, Austrian, I. 550*a*  
**Cinnamaldehyde**, III. 180*a*  
 — in cassia oil, II. 418*d*  
 — cinnamon, III. 183*b*  
**Cinnamein**, I. 616*c*  
**Cinnamic acid**, I. 196*a*; III. 180*c*  
 —, detection in butter, II. 167*d*  
 —, — food, V. 301*b*  
 —, —, detn., III. 181*a*  
 —, —, 3:4-dihydroxy-, II. 196*d*  
 —, —, in condensation reactions, III. 181*c*  
 —, —, *o*-nitro-, III. 181*d*  
 —, —, polymerisation, photo-effect, III. 181*b*  
 —, —, prepn., II. 361*d*  
**alloCinnamic acid**, III. 181*b*  
**Cinnamic acids**, *cis*-, and *trans*-, III. 181*b*  
 — alcohol, III. 181*d*  
**Cinnamomum camphora**, II. 240*d*; IV. 4*b*  
 — *cassia*, I. 11*d*  
 — spp., eugenol from, IV. 394*c*  
 —, —, methyl ether from, IV. 394*d*  
**Cinnamon**, III. 182*a*  
 — bark, essential oil, III. 183*a*  
 —, cinnamaldehyde in, III. 180*a*  
 — leaf, essential oil, III. 183*b*  
 — stone, III. 183*c*  
**Cinnamyl alcohol**, III. 180*c*, 181*d*  
 — esters, III. 181*d*  
**Cinobufagin**, II. 388*a*  
**Cinobufotoxin**, II. 388*b*  
**Cinogenic acid**, III. 179*b*  
 — "*Cisalfa*," V. 113*d*  
 — "*Citobaryum*," III. 183*c*  
**Citraconic anhydride**, III. 185*d*  
**Citral** in citron oil, III. 191*a*  
 —, reduction, II. 429*d*  
**Citrals**, III. 183*c*  
**cycloCitrals**, III. 184*b*  
**Citraptene** in citron oil, III. 191*a*  
**Citrates**, qualitative reactions, II. 570*b*  
**Citraurin**, II. 401*b*; III. 184*d*  
**Citric acid**, III. 185*a*  
 —, —, qualitative reactions, II. 570*b*  
**Citrinin**, V. 54*d*  
**Citromycetin**, V. 53*d*  
**Citron**, III. 190*c*  
 — (cedrat) oil, III. 190*d*  
**Citronella**, essential oil, III. 191*a*  
**Citronellal**, III. 184*b*, 191*c*  
 —, hydroxy-, VI. 401*d*  
**Citronellolic acid** in citronella oil, III. 191*b*  
**Citronelloil**, III. 184*b*, 192*b*  
 — in camphor oil, II. 249*b*  
 — production, II. 429*d*  
**Citronellyl esters**, III. 193*b*  
**Citronin**, VI. 80*d*  
**Citrulline**, I. 318*b*; III. 193*b*  
**Citrullus colocynthis**, III. 294*a*  
**Citrus**, VI. 90*a*  
 — *aurantium*, I. 683; III. 184*d*  
 — *decumana*, VI. 92*b*, 129*a*  
**Citrus juice**, III. 186*d*  
**Civet**, II. 174*d*; III. 193*c*  
**Civetone**, III. 194*b*  
**Claisen** condensation with boron trifluoride catalyst, VI. 259*d*  
 — reaction, II. 365*d*  
**Clarain**, V. 351*a*  
**Claret**, Caledon, R. I. 427*b*  
**Claricepsin**, IV. 331*d*  
**Clarifoil**, III. 194*b*  
**Clarit**, III. 194*b*  
**Claude** synthetic ammonia process, I. 337*c*  
**Claudetite**, I. 460*a*, 476*b*  
**Claus and Volz**, *o*-acid of, I. 658*c*  
**Clausnizer** and Wollney extractor, IV. 581*d*  
**Clausthalite**, III. 194*b*  
**Clauceps purpurea**, IV. 320*d*  
**Clavicepsin**, III. 194*b*; • IV. 331*d*  
**Clay**, III. 194*b*  
 —, blue, diamond-bearing, II. 309*b*  
 —, —, chemical analysis, III. 200*b*  
 —, —, -grog bricks, II. 360*d*  
 —, —, -iron-stone, II. 519*d*  
**Clayite**, III. 190*a*; 204*b*  
**Clay products** in building, II. 123*c*  
 —, —, slate, VI. 126*c*  
**Cleansing** in brewing, II. 100*c*  
**Clematine**, I. 577*a*  
**Cleveite**, II. 106*a*; III. 204*c*  
**Cleveland slag**, II. 145*a*  
**Cleve's acids**, III. 204*c*  
**Cliftonite**, II. 315*a*; III. 574*c*  
**Climbing film evaporator**, IV. 410*b*  
**Clouds**, particle sizes in, IV. 95*a*  
**Clove**, III. 204*c*  
**Clovene**, clovenic acid, II. 410*c*  
**isoClovene**, II. 410*c*  
**Clove oil**, IV. 394*c*  
 —, —, caryophyllene in, II. 408*d*  
**Clover**, III. 205*c*  
 —, crimson, glycoside in, VI. 90*b*  
 —, —, flowers, III. 206*a*  
 —, —, meal, IV. 596*b*  
**Cloves**, essential oil, III. 207*b*  
**Clupanodonic acid**, IV. 85*b*  
 —, —, reduction, VI. 225*a*  
**Clupeine**, I. 459*c*; III. 207*c*  
**Cnicin**, II. 480*c*  
**Coacervation**, III. 291*a*  
**Coagels**, III. 291*a*  
**Coagulation** of blood, II. 22*c*  
 —, —, hydrophilic sols, III. 286*b*  
 —, —, hydrophobic sols, III. 285*b*  
**Coal**, Admiralty steam, V. 343*b*  
 — analysis, rapid methods, I. 531*c*  
 — ash, V. 350*a*  
 —, —, composition, V. 449*c*  
 —, —, benzene extraction, V. 354*a*  
 —, blind, II. 13*a*  
 —, bright, V. 350*d*  
 — briquettes, V. 360*b*  
 —, caking index, V. 347*b*, f.n.  
 —, cannel, V. 347*b*, 437*c*  
 — carbonisation (see also Carbonisation; Coal, destructive distillation of; Coke manufacture; Fuel; Gas, coal; Gas, water), V. 351*c*  
 —, —, chemical changes in, V. 440*b*  
 —, —, continuous, in vertical retorts, V. 443*d*  
 —, —, high temperature equilibrium, V. 451*d*  
 —, —, high temperature products, V. 452*b*  
 —, —, in coke ovens, III. 260*d*; V. 446*c*  
 —, —, inclined retorts, V. 443*a*  
 —, —, intermittent, in vertical retorts, V. 443*b*  
 —, —, producer gas heating in, V. 430*d*  
 —, —, primary decomposition in, V. 449*c*  
 —, —, retorts, horizontal, V. 439*a*  
 —, —, secondary decomposition in, V. 451*a*  
 —, —, to active charcoal, II. 310*a*  
 —, —, chemical composition, V. 335*c*, 319*b*  
 —, —, classification, V. 340*c*  
 —, —, composition and constitution, V. 349*b*, 350*a*  
 —, —, critical temperature, V. 352*c*  
 —, —, decomposition point, V. 352*c*  
 —, —, products, nitrogen in, V. 353*a*  
 —, —, sulphur in, V. 353*b*  
 —, —, destructive distillation of (see also Coal carbonisation; Coke manufacture; Fuel; Gas, coal), II. 344*d*  
 —, —, dull, V. 350*d*  
 —, —, dust explosions, IV. 108*b*  
 —, —, efficient combustion, V. 359*a*  
 —, —, extraction with solvents, V. 353*c*  
 —, —, extrinsic mineral matter in, V. 340*d*  
 —, —, fields, British, V. 344*b*  
 —, —, of Germany and Poland, V. 347*c*  
 —, —, of U.S.A., V. 347*d*  
 —, —, flotation, V. 268*a*  
 —, —, formation, V. 335*c*, 335*b*  
 —, —, gas, see Gas, coal.  
 —, —, gasification, V. 351*c*, 367*c*, 472*d*  
 —, —, geographical distribution, V. 333*d*, 344*b*  
 —, —, hydrogenation, II. 425*d*; VI. 364*c*, 371*c*  
 —, —, Bergius plant for liquid phase, VI. 365*d*  
 —, —, catalysts, VI. 368*a*  
 —, —, vapour phase treatment of middle oil, VI. 365*d*

- Coal**, intrinsic mineral matter in, V. 349*d*  
**"Coalite"** process, V. 365*c*  
 —, oils from, III. 423*d*; V. 365*d*  
**Coal**, liquid fuels from, V. 378*a*  
 —, "mineral charcoal" in, V. 350*d*  
**"Coal"**, mother of, V. 350*d*  
**Coal**, nitrogen content, I. 339*a*; V. 350*c*  
 —, occluded gas in, V. 349*c*  
 —, occurrence, V. 333  
 —, oil mixtures as fuel, V. 364*a*  
 —, "oil point", V. 351*d*  
 —, parrot or cannel, V. 347*b*, 437*c*  
 —, pulverised, V. 361*a*  
 —, —, in Diesel engines, V. 303*b*  
**Coals**, anthracitic, V. 340*a*  
 —, bituminous and semi-bituminous, V. 340*a*  
 —, brown, V. 338*c*  
 —, classifications, V. 340*c*, 437*c*  
**Coal**, spontaneous ignition, V. 357*d*  
**Coals**, steam, V. 437*c*  
 —, sub-bituminous, V. 338*c*  
**Coal** storage and self-ignition, V. 357*d*  
 — substance, degradation, V. 355*c*  
 — —, thermal decomposition, V. 351*c*  
**Coal** tar, III. 207*c*, 262*b*, 264*b*  
 — —, analysis, III. 214*a*  
 — —, benzole for motor spirit, III. 212*c*  
 — —, inhibiting gun formation in, III. 212*c*, 267*d*  
 — —, carcinogenic action, II. 378*b*  
 — —, constituents, III. 207*c*, 208*a*  
 — —, Dillamore tower, V. 447  
 — —, distillation, III. 209*a*  
 — —, fractions, anthracene oil, III. 211*b*  
 — —, benzole, III. 211*b*  
 — —, carboic oil, III. 211*b*  
 — —, cresote oil, III. 211*d*  
 — —, light oil, III. 211*b*  
 — —, middle oil, III. 211*b*  
 — —, naphthalene, III. 212*d*  
 — —, phenols, III. 212*d*  
 — —, pitch, III. 212*d*  
 — —, resinoids, III. 212*d*  
 — —, in road construction, III. 213*a*  
 — —, output from low temperature carbonisation, V. 365*a*  
 — —, in gas manufacture, V. 453*a*  
 — —, pipe still, III. 210*c*, 211*a*  
 — —, pitch, III. 208*b*, 212*a*  
 — —, pot still, III. 209*c*  
 — —, tars, hydrogenation, I.C.I. plant, VI. 371*d*  
 — —, ulmins, V. 353*a*  
 — —, valuation, V. 357*a*  
**Coating** compositions, emulsions for, IV. 302*d*  
**Cobalt**, III. 214*b*  
 — alloys, III. 104*c*, 216*c*  
 — aluminote, II. 25*b*  
**Cobaltamine** salts, III. 221*b*, 330*a*–335*b*  
**Cobalt ammonium** phosphate, III. 219*b*  
 — antimonides, III. 220*d*  
 — arsenate, hydrated, III. 214*b*  
 — arsenides, III. 220*c*  
 — as trace element, I. 505*d*  
 — black earthy, III. 214*b*  
 — bloom, I. 469*a*; III. 214*b*, 222*c*; IV. 335*c*  
 — carbide, II. 281*c*  
 — carbonyls, II. 357*a*; III. 220*d*  
 — catalyst in cracking processes, III. 217*d*  
 — complexes with catechol, II. 431*a*  
 —, detn., assay, I. 523*a*  
 — —, colorimetric, II. 671*a*  
 — —, electrodeposition method, II. 700*d*  
 — —, gravimetric, II. 612*a*  
 — —, volumetric, II. 656*a*  
 — driers, III. 222*a*  
 —, drop reaction, II. 580*b*  
 —, electrodeposition, III. 217*d*; IV. 266*d*  
 — extraction, III. 214*c*, 216*a*  
 — glance, III. 214*b*, 222*c*  
 — hydroxides, III. 218*a*  
**Cobaltic** oxide, III. 218*a*  
**Cobalt** in enamels, III. 220*c*  
**Cobaltite**, I. 469*a*; III. 214*b*, 222*c*  
**Cobalt "linoleate"**, III. 222*b*  
 — matte, III. 214*d*  
 — nitrate, dry reactions, II. 548*a*  
 — nitrides, III. 220*d*  
**Cobalto-cobaltic** oxide ( $\text{Co}_3\text{O}_4$ ), III. 218*a*  
**Cobalt** ores, III. 214*c*  
**Cobaltous** oxide, III. 218*a*  
**Cobalt** oxide catalyst for oxidation of carbon monoxide, II. 317*a*  
 — — in motor fuel production from water gas, II. 425*d*  
 — — production of olefins, II. 350*d*  
 — — in ceramics, III. 220*a*  
 — — glassmaking, II. 558*c*, 561*c*, 565*a*  
 — pigments, III. 218*c*  
 — properties, III. 216*a*  
 — pyrites, III. 214*b*  
 — qualitative reactions, II. 548*c*, 552*d*, 553*a*, 578*a*  
 — —, rare metals present, II. 554*a*, 550*d*  
 — resinate, prepn., III. 222*a*  
 — salts, III. 221*b*  
 — silicides, III. 220*d*  
 — smelting, III. 214*d*  
 — speiss, III. 214*d*, 219*d*  
 — sulpharsenide, III. 214*b*, 222*c*  
 — sulphates, III. 221*c*  
 — sulphides, III. 220*c*  
 — stannate, II. 25*a*  
 — "lungate," III. 222*a*  
**Cobb's** process, I. 341*a*  
**"Coblac"**, II. 480*a*  
**Cocaine** and alkaloids of Erythroxyllum species, I. 369*a*; III. 222*d*, 224*a*  
 —,  $\gamma$ - and  $\delta$ -isotropyl-, III. 222*d*  
 — borate, II. 50*c*  
 —, cinnamoyl-, III. 222*d*, 224*c*  
 — group, physiological action, III. 226*b*  
**Cocaines**, constitution, III. 225*a*  
 —, syntheses, III. 225*b*  
**Coca** leaves, analyses, III. 223*d*  
 —, export, III. 223*a*  
 —, extraction, III. 223*b*  
**Cocamine**, isococamine, III. 224*c*  
**Co-carboxylase**, V. 18*c*  
**Cocceric** acid and coccerinic acid, III. 230*b*  
**Coccerin**, III. 230*b*  
**Cocceryl** alcohol, III. 230*b*  
 $\alpha$ -**Coccinic** acid, III. 228*b*  
**Coccinin**, coccinone, III. 228*d*  
**Cocculin**, I. 370*a*  
**Cocculus indicus**, *C. spp.*, I. 370*a*; III. 230*c*, 460*b*; IV. 52*d*  
**Coccus cacti**, III. 226*c*  
**Cochenillic** acid, III. 228*b*  
**Cochin** China wax, IV. 4*a*  
**Cochlearia armoracia**, VI. 96*a*, 280*d*  
**"Cochin** oil," III. 239*b*  
**Cochineal**, III. 226*c*; IV. 126*b*  
 —, dyeing properties, III. 230*a*  
 —, fat and wax, III. 230*b*  
 — indicator, II. 639*d*  
**Cocinic** acid, III. 230*c*  
**Coclaurine**, III. 230*c*  
**Cocoa** (cacao), III. 230*d*  
 — albuminoids, III. 235*d*  
 — alkaloids, II. 197*a*  
 — Brown, III. 236*a*  
 — butter, II. 159*c*, 183*d*; III. 233*b*  
 —, adulteration, analysis, III. 234*a*  
 — fermentation, III. 231*c*, 232*a*  
 —, mineral matter in, III. 230*c*  
**Cocoanut**, see Coconut  
**Cocoa** plum, VI. 410*c*  
 — Red, III. 236*a*  
 —, roasted nib, III. 233*c*  
 — shell, III. 236*c*  
**Cocoas**, soluble, III. 232*d*  
**Cocoa** starch, III. 236*a*  
 — tannin, III. 236*a*  
**Coconut**, III. 237*a*  
 — butter, II. 159*c*  
 — oil as adulterant in cacao butter, II. 187*a*  
 — group, III. 238*a*  
 — in chocolate, III. 88*c*  
 — press cake, III. 240*b*  
 — oils, analyses, III. 240*a*  
 — oil, wax from, III. 240*d*  
 — olein, III. 242*b*  
 — parings oil, III. 241*a*  
**"Coconut** ponac," III. 239*b*  
**Coconut** stearin, III. 242*a*  
 — as adulterant in cacao butter, II. 187*a*  
 — in candles, II. 264*b*  
**Cocositol**, III. 244*b*; VI. 495*d*  
**Cocos nucifera**, *C. spp.*, III. 237*a*, 238*c*, 244*b*  
**Codamine**, III. 244*b*  
**Co-dehydrogenase**, I and II, V. 15*d*, 16*a*  
**Codeine**, III. 244*c*  
 —, acetyl-, I. 12*c*  
 — methylbromide, IV. 392*b*  
**Codeinone**, dihydroxy-, hydrochloride, IV. 400*b*  
**"Codeonal"**, III. 244*c*  
**Cod-liver** oil, III. 244*c*  
 — as feeding stuff, IV. 597*b*

- Cod-liver** oil, emulsification, II. 403c  
— oil, *see* Cod-liver oil.
- Coelestine**, III. 250c
- Cœlin-blau**, II. 25a
- Co-enzyme** factor, V. 34b
- Co-enzymes**, III. 250c; V. 15b; VI. 75b  
— of alcoholic fermentation, V. 15b; VI. 74a
- Cœrulein**, I. 229c  
— B and S, I. 229d
- Cœruleum**, II. 25a
- Cœrulignone**, II. 440d
- Coffea arabica**, *C. pauciflora*, III. 251b, c
- Coffee**, III. 251b  
—, adulteration, III. 255c  
—, alkaloids, II. 197a  
—, bean oil and wax, III. 257c  
—, decaffeinated, III. 257a  
—, detection of chicory in, III. 256a  
—, substitutes, III. 257b
- Coffey** still, I. 176d
- Cognac**, II. 63b  
"Cognac oil," II. 63b
- Cogon** grass, II. 497c  
"Cogwheel-ore," II. 53d
- Cohenite**, II. 280c, 480c
- Cohosh**, Black, I. 137a
- Cohne** nut, III. 257d  
— oil, III. 213d
- Coir**, III. 239a, 258a; V. 158d
- Coke** manufacture and the recovery of by-products (*see also* Carbonisation: Coal carbonisation; Fuel; Gas, coal; Gas, water), III. 258c  
— oven gas utilisation, I. 335a; III. 268d  
— ovens and by-product recovery, III. 258c  
—, semi-, V. 301d, 307a  
—, vertical retort, dense, V. 443c, 446b
- Cola-catechin**, II. 438d
- Colamine**, III. 94a
- Colburn** and Lobbey-Owens window-glass drawing machine, V. 593b
- Colchicine**, III. 277c
- Colchicine** acid, III. 278a
- Colchicum** and colchicine, III. 276b  
—, *Liliaceae* spp. containing, III. 276c  
—, physiological action, III. 278b
- Colcothar** (*see also* Caput mortuum), III. 278c
- Colemanite**, borax manufacture from, II. 40a, 40d, 49b  
—, boron mineral, II. 30c, 35b, 48c; III. 278c
- Collagen**, II. 27b; V. 501b; VI. 21b  
"Collargol," III. 278d, 288a
- Collectors** (flotation process), V. 263d, 267a
- Collidine** from acetylene and ammonia, I. 84c
- Collidines**, III. 278d; IV. 378a
- Collin**, III. 278d  
"Colliron," III. 278d
- Collision** number in a gas, VI. 227b  
— the liquid phase, VI. 220d
- Collodion**, II. 446b, 468b  
—, coating on photographic film, II. 450a  
— cotton (*see also* Nitrocellulose), II. 467d; IV. 516b  
—, flexible, II. 261a  
—, lacquers, II. 468d
- Colloidium**, *see* Collodion.
- Colloidal** fuel, V. 364a  
— particles, size and shape, I. 160a; III. 288d, 289a
- Colloid** dispersion by solubility reduction, III. 281a  
— solvent change, III. 281a  
— dispersions, III. 279d  
— equivalent, III. 281d  
— formation by chemical reaction, III. 281b  
— simultaneous condensation, III. 281b  
— milks, III. 280d; IV. 298a  
— stability, III. 281d
- Colloids**, III. 278d  
—, caseinate, II. 116  
—, electrical properties, III. 283b  
—, gold numbers, III. 287b  
—, hydrophilic, III. 279d, 286b, 291d  
—, autoprotection, III. 292d  
—, effect on solubility, crystallisation and chemical reaction, III. 292d  
—, hydrophobic, III. 279d, 281b, 285b  
—, lyophilic, III. 279d  
—, lyophobic, III. 279d  
—, mechanical dispersion, III. 280d; IV. 298a  
—, osmotic pressure, III. 288a  
—, peptisation, III. 281a  
—, prepn., III. 280d  
—, purification by dialysis, III. 281c
- Collophanite**, III. 294a  
"Colloresin," II. 180a  
"Colloresin DK," IV. 178c  
— in calico printing, IV. 180d
- Colocynth** (*colocynthis*), III. 294a
- Cologne** earth, III. 456a
- Colophony**, I. 2a; III. 294b  
"Coloran B," III. 295d
- Colorimeters** and colour comparators, III. 295d  
—, Autenrieth - Königsberger, III. 304b  
—, Donaldson, III. 298b  
—, Duboseq, III. 303d  
—, Eastman, III. 303b  
—, Guild, III. 297d  
—, Lovibond, III. 302b  
—, Nutting, III. 301c  
—, Ostwald, III. 301c  
—, Patterson, III. 303d  
—, Prest, III. 301c  
—, Pulfrich or Stupho, III. 304d  
—, Richter, III. 298d  
—, Schreiner, III. 303d  
—, Van den Bergh-Groetepass, III. 304c  
—, Wright, III. 298d
- Colorimetric** analysis, II. 669b
- Colorimetry**, photoelectric cells in, III. 300c, 305c  
—, trichromatic coefficients, III. 296d
- Colour** and chemical constitution, III. 306b  
— quality, III. 296d
- Columbamine**, II. 235b
- Columbin**, II. 235b
- Columbite**, III. 309c
- Columbium** (niobium), III. 309d
- Combustion**, effect of water vapour, V. 237a  
—, photo-sensitisation, IV. 418b  
—, pre-flame, IV. 417b  
—, slow, IV. 417c  
—, of simpler hydrocarbons, IV. 418c, 419b
- Comenic** acid, V. 48c
- Comfrey**, III. 313c
- Commelina communis**, I. 560c; III. 551c
- Commiphora** spp. gum resin, I. 658c
- Composition** exploding, IV. 483a  
"Compound" (hard), IV. 253b
- Compound** cakes and meals, IV. 535d
- "Compral," III. 313c
- Conarachin**, I. 454c
- Conchairamidine**, III. 128a, 160a
- Conchairamine**, III. 128a, 160b
- Concrete**, II. 117a
- Concusconine**, III. 128a, 160c
- Condensation**, types of, III. 321a
- Condensers**, III. 313d  
— for metal vapours, III. 320a  
—, history, III. 313d  
—, jet, large-scale, III. 319c  
—, laboratory, double surface, III. 310d  
—, types, III. 310a  
—, reflux, III. 318b, 321b  
—, surface, large-scale, III. 319a  
—, theory, III. 320c
- Condurango**, conduragin, III. 321c
- Conduransterin**, III. 321d
- Conduritol**, III. 321c
- Condurrite**, IV. 55c
- Condys** fluid, III. 321d
- Conessidine**, III. 322c, 323b
- Conessimine**, conconessimine, III. 322a, b, d, 323a
- Conessine**, III. 321d  
apoConessine, III. 324a
- Conglutin**, III. 324b
- Conhydrine**, III. 324b, d, 325b, pseudoConhydrine, III. 325a, 320a
- Coniceles**, III. 324d, 325c
- Coniferin**, III. 324b
- Coniine**, d- and l-, III. 325a  
Coninum purum, III. 324d
- Conimine**, III. 322d, 323b
- Conium** alkaloids, III. 324c
- Conium maculatum**, III. 324c
- Conkurchine**, III. 323b
- Connellite**, III. 326b  
—, relation to buttgembachite, II. 168d
- Conquinamine**, III. 128a, 160c
- Conquinine**, III. 169b
- Conrady** method of weighing, I. 613c
- Constantan**, III. 326c  
"Construal," I. 277a

- Contact angles**, V. 284a; VI. 506d
- Continuous phase**, III. 279b
- "Contramine,"** III. 326c
- Convallamarin**, II. 387a; III. 326c
- Convallaria majalis**, glycosides II. 387a; III. 326c
- Convallarin**, II. 387a; III. 326c
- Convallatoxin**, II. 387b
- Convergence temperature**, III. 443b
- Convicine**, III. 326c; VI. 80d
- Convulamine**, III. 327a
- Convulicine**, III. 327b
- Convulvidine**, III. 327b
- Convolve**, III. 327a
- Convolvulin**, III. 326c; VI. 87a
- Convolvulus batatas**, I. 655d
- *orizabensis*, VI. 90c
- *pseudocrotabricus*, alkaloids of, III. 326d
- Conyrine**, III. 325c
- Cooking fats**, IV. 253a
- Cook's alloy**, III. 327c
- Cool flames**, IV. 422c
- Cooperite**, minerals and alloy, II. 327c
- Cooppal's powder**, IV. 519a
- Co-ordination compounds**, III. 327c
- — — in chemical analysis, III. 335a
- — —, isomorphism, III. 334d
- — —, mordant dyes, III. 335b
- — —, octahedral structure, III. 330b
- — —, planar structure, III. 332a
- — —, polynuclear, III. 333b
- — —, tetrahedral structure, III. 331a
- — — covalency, III. 331b; IV. 273b
- — —, electronic interpretation, III. 333d
- — — in physiology, chlorophyll, III. 336d
- — —, haemin, III. 336c
- — —, hæmocyamine, III. 336c
- — —, turacin, III. 336d
- — — number, 3, 5, 7, III. 333d
- — —, 4, 6, III. 330a
- — —, 8, III. 333c
- — — of hydrogen, supposed, IV. 274c
- — — manifold associating groups, III. 328b
- — —, stereochemical demonstration, III. 330a
- Copaene**, III. 337a
- Copalba**, III. 337b
- , essential oil, III. 338b
- Copaifera spp.** products, oils and resins, III. 387-340
- Copaivic acid**, III. 337d
- Copal**, III. 338d
- , Accra, I. 12c
- Copalin**, III. 340d
- Copal**, New Zealand, III. 340a
- Copals** in order of hardness, III. 340c
- Co-pigments**, III. 340d
- Copper**, III. 341c
- acetoarsenite, I. 478a
- acetylides, I. 82a; II. 281b; III. 356b
- — aluminium, equilibrium diagram, VI. 282a
- ammonium lactate, absorption of carbon monoxide by, II. 351b
- and its alloys, uses, III. 353a
- , antimonial, I. 439d
- , antimony as impurity in, III. 352d
- , — with arsenic as impurities in, III. 352c
- , arsenic as impurity in, III. 351d
- , — and arsenic as impurities in, III. 352a
- arsenides, III. 355c
- as chlorine carrier, II. 351b
- — trace element, I. 506a
- , bismuth as impurity in, III. 352b
- , black oxide, III. 351b
- , blast-furnace smelting, III. 344c
- carbonate, mineral, III. 26c
- catalyst in oxidation of sulphates, VI. 260d
- — — Tiemann-Reimer reaction, II. 364c
- chromium alloy, III. 104a
- compounds, *see also* Cupric and cuprous compounds.
- cyanide, III. 485d
- detn., assay, I. 523a
- by electrodeposition, II. 700d
- , colorimetric, II. 671b
- , gravimetric, II. 580b
- , —, micro, II. 633c
- in food, V. 202d
- , potentiometric, II. 707b
- , spectroscopic, II. 692a
- , volumetric, II. 656c
- drop reactions, II. 580c
- electrodeposition and plating, IV. 262b
- extraction, dry methods, III. 342a, c
- , wet methods, III. 349b
- , formation of carbonyls catalysed by, II. 357b
- glance, II. 517c
- , artificial, III. 355a
- , ore, II. 517c; III. 311c
- hydroxide as pigment, II. 25c
- in Reformatsky reaction, II. 366b
- rice, II. 406b
- , iron as impurity in, III. 352b
- matte, crude copper from, III. 346d
- monoxide, III. 354b
- , native, III. 341c
- number of cellulose, *see* Cotton, copper number.
- , occurrence, III. 341c
- ore, azure, I. 583d
- , peacock, II. 517c
- , pitchy, III. 119b
- oxide catalyst for olefin production, II. 350d
- — — hydrogen production from water gas, II. 349b
- in respirators, III. 19b
- , oxidation of carbon monoxide by, II. 347a, 351c
- Copper oxides**, III. 353c
- oxychloride as pigment, II. 119b
- , oxygen as impurity in, III. 351d
- peroxide, III. 353d
- , phosphorus as impurity in, III. 352d
- pyrites, II. 517c; III. 341c
- , pyritic smelting, III. 345a
- , qualitative dry reactions, II. 547c, 548a
- , — reactions, II. 551c, 560b
- , —, rare metals present, II. 554c, 556d
- , red oxide, III. 353d
- , refining, III. 348b, d
- , electrolytic, III. 348d; IV. 264b
- , reverberatory-furnace smelting, III. 345c
- salts, ammoniacal, for absorption of carbon monoxide, II. 349b
- as disinfectants, IV. 24d
- — pigments, II. 86a
- silicate, artificial, III. 119b
- , —, mineral, III. 355c
- silicide, III. 355d
- smelting, Bessemer process, III. 347c
- for matte, III. 342d
- suboxide, III. 353d
- sulphantimonite, II. 53d
- sulpharsenate, IV. 307d
- sulphate (*see also* Copper vitriol), III. 357b; VI. 298a
- , agricultural, III. 357c, 358b
- as algicide, I. 201b
- — fungicide, II. 30d
- , —, basic, mineral, II. 106a
- in respirators, III. 20c
- , native, II. 517a
- in alloys, IV. 270d
- uroporphyrin, VI. 164c
- vessels in methanol synthesis, II. 350b
- vitriol (*see also* Cupric sulphate), II. 517a; III. 341c
- zinc, equilibrium diagram, VI. 281d
- Copra**, copra oil, III. 237b, 239c, 243a
- Coprolites** for superphosphate manufacture, III. 359a; V. 69a
- Copromesobiliviolin**, I. 692a
- Copronigrin**, I. 692a
- Coproporphyrin**, VI. 162a
- Coprosma spp.**, III. 359b
- Coprostanol**, III. 89b
- Coprostanone**, III. 91c
- Coprostenone**, III. 91c
- Coprosterol**, III. 89b, 91c
- Coptisine**, III. 359b
- Coptis japonica**, III. 359b
- Coracan**, II. 488d
- Coral**, III. 360c
- Coral-ore**, III. 180a
- Coralydine**, I. 35a
- "Coramine"** (Ciba), III. 361b
- Corchorus spp.**, V. 163b
- Cordeau detonant**, III. 316b
- Cordials**, III. 361b
- Cordite**, III. 361d; IV. 518b
- , analysis, III. 363c
- R.D.B., III. 364a
- Cordylite**, III. 364a
- Coréopaine** pour cuir, I. 133b

- Coriander**, III. 364b  
 —, essential oil, III. 364d  
**Coriandrol**, III. 364d  
*Coriandrum sativum*, III. 364b  
**Cori ester**, V. 36c; VI. 77d  
 —, catalysis by magnesium ions, VI. 77d  
**Corindite**, III. 365a  
**Corinth RK**, I. 420a  
**Corioflavines**, I. 133d  
**Coriphosphin O** and BG, J. 132b  
**Cork**, III. 365b  
 — dust in plastics, II. 470a  
 — in casein glues, II. 415b  
**Corning lamp-bulb machine**, V. 588a  
**Cornish stone**, III. 32b  
**Corn oil**, II. 482a  
 — parsley, VI. 262c  
**Cornuite**, III. 119b  
*Coronilla scorpioides*, *C. varia*, III. 306c  
**Coronillin**, II. 387d; III. 366c  
**Corozo**, III. 366c  
**Corrosion**, agent in prevention, VI. 300a  
 — fatigue, III. 379d  
 — of immersed metals, III. 375a  
 — — — and electrode potential, III. 375b, 380a, 396c  
 — — — metals, III. 366c  
 — — —, anodic oxidation against, I. 254b; III. 392b  
 — — —, atmospheric, III. 368a  
 — — —, bituminous coatings for prevention, III. 395d  
 — — — by carbon tetrachloride, II. 356d  
 — — — sea water, III. 381a  
 — — — soils, III. 384b  
 — — —, cementation processes for prevention, III. 397a  
 — — —, differential aeration principle, III. 379a  
 — — —, effect of oxygen supply on, III. 378b  
 — — —, electrochemical control, III. 387d  
 — — —, electrodeposited coatings for prevention, III. 397b  
 — — —, grease coatings and slushing compounds for prevention, III. 394d  
 — — —, hot-dipping for prevention, III. 396b  
 — — — in refrigerating systems, III. 387d  
 — — — the open air, III. 372d  
 — — —, inhibitors for prevention, III. 386a  
 — — —, lacquers and varnishes for prevention, II. 467d; III. 394d  
 — — —, metal-cladding for prevention, III. 396b  
 — — —, coatings for prevention, III. 396a  
 — — —, spray processes for prevention, III. 397a  
 — — —, paint and allied coatings for prevention, III. 393b  
 — — —, protection by control of external factors, III. 385c  
**Corrosion** of metals, protection of ships' hulls against, III. 382a  
 — — —, protective measures, III. 385c  
 — — —, "rolled-on coatings" for prevention, III. 396b  
 — — —, season-cracking in, III. 380d  
 — — —,terne plate for prevention, III. 396d  
 — — —, testing protective metallic coatings, III. 398a  
 — — —, resistant alloys, aluminium bronzes, III. 390a  
 — — —, — magnesium, I. 250a, 251a; III. 390b  
 — — —, brass, III. 389d  
 — — —, bronze, III. 390a  
 — — —, copper-rich, III. 389c  
 — — —, iron-rich, III. 388b  
 — — —, nickel-rich, III. 388a  
**Corrosive sublimate**, III. 398b  
**Corsite**, IV. 8b  
**Corticinic acid**, III. 366b  
**Corticosterone**, VI. 277b, c  
**Corticin activity**, VI. 277b, 278c  
**"Corubin,"** I. 4b; III. 399c  
**Corundum**, abrasive, I. 4a; II. 359a; III. 399b  
 —, artificial, III. 399c; V. 512d  
 —, —, for gems, III. 399b  
 —, mineral, I. 204c; III. 398b  
**Corybulbine** and isocorybulbine, III. 401c  
**Corycavamine**, III. 402c  
**Corycavidine**, III. 402c  
**Corycavine**, III. 402b  
*pseudocorycavine*, III. 402d  
**Corydaldine** formation, II. 236a; III. 401b  
**Corydaline**, III. 400d  
*Corydalis* spp., alkaloids, III. 399d  
*Corydalis tuberosa*, VI. 1a  
**Corydine** and isocorydine, III. 403a, b  
**Corylin**, V. 180c  
*Corylus* spp., V. 180b; VI. 189d  
**Corynanthine**, III. 403d  
**Corypalmine**, II. 236b; III. 402b  
**Corytuberine**, III. 403a  
**Costenes**,  $\alpha$ - and  $\beta$ -, III. 403d  
**Costol**, III. 403d  
**Costus**, essential oil, III. 404a  
**Cotarnine**, III. 404a  
**Coto bark**, III. 404a  
**Cotoin**, III. 404a  
 —, di-, hydro-, methylhydro-, methylproto-, and proto-, III. 404a  
**Cotton** (see also Bleaching; Cellulose; Dyeing; Explosives), V. 135a  
 —, acetylated to resist substantive dyes, V. 191b  
 — anthracnose, V. 139a  
 — ash, composition, V. 142d  
 — bleaching, II. 3c  
 —, hypochlorite, II. 3a, 5a, 10a  
 —, peroxide, II. 10c  
 — blowing room, V. 144d  
 — carding, V. 140b  
 — cellulose (see also Cotton), II. 4b, 462b; V. 141b  
 —, chain length, II. 301d, 458a  
**Cotton cloth**, see under Bleaching; Finishing textile fabrics; Fabrics.  
 — combing and drawing, V. 149a  
 —, copper number, II. 463a; IV. 507c; V. 143a  
 —, Devil's, I. 4c  
 — fibres, V. 135a  
 — flowers, III. 405a  
 — ginning and pressing, V. 143d  
 — grey, composition, II. 3d  
 — growing, diseases, pests, yield, V. 138a  
 — lint hairs, V. 139c  
 — opening and cleaning, V. 144c  
 —, properties of non-cellulose constituents, II. 4c  
 —, proteins, V. 142b  
 — quality, tests, V. 140b  
 — rayon cloth, effect of alkali-boil, V. 184a  
 — rovings, V. 149d  
 —, scouring and chemicking, continuous systems, II. 9d  
**Cottonseed cake**, I. 455a; III. 400d  
 —, colouring matter, III. 407b  
 — oil, III. 408d  
 —, analytical limits, III. 410d  
 —, hardening, II. 426d; VI. 183c  
 —, hydrogenated, III. 410c; VI. 183c  
**Cotton singles**, V. 151c  
 — sliver, V. 149a  
 — spinning, V. 144a, 150a  
 — thread, V. 151c  
 — warp beam, V. 152d  
 — wax, V. 141d  
 — weft, V. 152a  
 —, white Egyptian, I. 1c  
 — wilt, V. 138d  
 — yarn preparation, V. 151b  
 — yarns, count, V. 144a  
**Couch grass**, I. 171d; III. 411d  
*Couepia grandiflora*, IV. 84a, 258a  
**Couepic acid**, IV. 258a  
**o-Coumaraldehyde** methyl ether in cassia oil, II. 418d  
**Coumaran**, III. 411d  
**Coumarin**, III. 412a  
 — glycosides, III. 412d  
 — in cassia oil, II. 418d  
**Coumarone**, III. 413a  
 — resins, III. 413b  
**Coupling** components, III. 583b; IV. 195d, 196d, 230d  
**Court plaster**, V. 508b  
**Covalency**, III. 334a; IV. 273a  
**Covellite** or covellite, III. 341c, 355b, 413d  
**Cowberry**, III. 414d  
**Cow pea**, III. 413d  
 — tree, II. 118a  
**"Coxpyria,"** I. 517d  
**Co-zyrnase**, II. 99d; III. 250c; V. 15b; VI. 78c  
 —, constitution, V. 17a  
 —, enzymic reduction, V. 16d  
 —, function, V. 32d  
 —, properties, V. 17b  
 —, reduction by hyposulphite, V. 16c

- "Crab's eye," I. 4c  
**Crabwood** oil, II. 277b  
**Cracklings**, VI. 135a  
**Cranberry**, III. 414b  
 —, American, VI. 92d  
**Crataegus spp.**, VI. 189b  
**Crazing** (pottery), VI. 12b  
**Creaming** of linen, II. 11d  
**Cream** of Tartar, III. 415a  
**Crease-resistant** cloth, V. 191c  
 —, resisting effects, V. 198c  
**Creatine**, III. 415a  
 —, and creatinine, VI. 144c  
 —, colour reaction, III. 416b  
 —, detn., III. 416b  
 —, homologues, III. 416b  
 —, phosphoric acid in muscle extract, VI. 75b  
**Creatinine**, III. 416d  
 —, detection, III. 417d  
 —, detn., Folin's method, III. 418b  
**Crenilabrine**, I. 450c  
**Creoline**, III. 419a  
**Creosol**, III. 419a  
 "Creosotal," III. 419a  
**Creosote**, III. 419b  
 —, as benzole wash-oil, III. 422d  
 —, blast-furnace, III. 421a  
 —, buck oil, III. 423c  
 —, coal-tar, III. 426b  
 —, —, specifications, III. 421c  
 —, Diesel oil, III. 423d  
 —, disinfectants and sheep dips, III. 422a, 424a  
 —, for preserving timber, III. 421a  
 —, fuel oil for furnaces, III. 422a  
 —, internal combustion engines, III. 422b, 423d  
 —, greases, III. 423b  
 —, in flotation processes, III. 423b  
 —, low temperature tar, III. 423c  
 —, oils, hydrogenation, II. 426b; III. 423a  
 —, timber-preserving oil, specification, III. 423d  
 —, water-gas tar, III. 424a  
 —, wood-tar, III. 419c  
 —, —, pharmaceutical, III. 420a  
**Cresatin**, III. 424b  
**Cresogol**, IV. 257c  
**Cresol** compounds in perfumery, III. 425d  
 —, disinfectants, III. 425c  
 —, in cascarilla oil, II. 411a  
**m-Cresol** in cresylic acid, III. 427b  
 —, 2:4:6-trinitro-, III. 428a  
**Cresols**, III. 424b, 427a, b  
 —, from coal, II. 304a  
**Cresolsulphonate**, nitro-, explosives, IV. 483d  
**Cresotic acid**, III. 425d  
**Cresotinic acid** (Kresotinsäure), III. 425d  
**Cresyl ether**, III. 426a  
**Cresylic acid**, II. 304a; III. 426b  
 —, recovery, II. 304b  
 —, specifications, analysis, III. 426c, d  
**Cresylite**, III. 425c, 428a  
**o-Cresyl phosphate**, III. 425c  
**Crin végétal**, I. 181a; V. 188b  
 "Crisaline," III. 428a  
**Crismer** test of butter, II. 166d  
**Cristobalite**, III. 428b  
**Crith**, III. 428c  
**Croceic acid**, I. 658c  
**Crocein acid**, I. 658c; III. 428c; IV. 208d  
**Crocetin**, II. 398d, 401b  
 —, and crocin, III. 428c  
 —, identity with nycanthum, II. 440a  
**Crocidolite**, I. 499c; III. 429d  
**Crocine**, III. 428c  
 **$\alpha$ -Crocin**, gentiobiose m, II. 200b  
**Crocoite** or **Crocorsite**, II. 96b; III. 430a  
**Crocus** of Antimony, I. 417b  
**Crocus spp.**, III. 428c; VI. 93d  
**Cronstedtite**, III. 430b  
**Crookesite**, III. 430b  
**Crops**, III. 430b  
 —, grass, III. 431b  
 —, legumes, III. 432c  
 —, root, III. 432a  
**Crossater paposus**, I. 532b  
 —, as teric acid m, I. 532b  
**Crotine**, III. 431b  
**Crotionalbumin**, III. 431b  
**Crotonaldehyde**, I. 26c, 27a  
 —, ethylacetal, I. 36b  
 —, formation, II. 423b  
 —, reduction, II. 426d  
**Crotonbetaine**, I. 450d; II. 391d  
**Crotonchloral hydrate**, II. 179b  
**Crotoglobulin**, III. 431b  
**Crotonitrile**, I. 258b  
**Croton** "Naturgiftstoff," III. 431c  
**Croton oil**, III. 434a  
 "Crotonoleic acid," III. 431d  
**Crotonoside**, III. 434b  
**Croton resin**, III. 431c  
**Croton tiglium**, III. 434a  
**Crotonylene**, I. 119c  
**Crotophorbolone**, III. 434d, foot-note  
**Crotyl alcohol**, conversion into butadiene, II. 154b  
**Crowberry**, III. 435c  
**Crucibles**, III. 435c  
 alumina, III. 439a  
 carbonaceous, III. 437b  
 "Carborandum," III. 439b  
 clay, III. 436d  
 Colorado, I. 520c  
 Cornish, III. 437a  
 French, III. 437b  
 graphite, III. 437c  
 Hessian, III. 437b  
 lime, III. 439d  
 London, III. 437a  
 magnesia, III. 439d  
 silica, III. 437b  
 —, white fluxing pots, III. 437a  
**Crude fibre** in feeding stuffs, IV. 593a, 602c  
**Crushed steel**, I. 3d  
 "Cryogenine," III. 440b  
**Cryolite**, artificial, I. 286b  
 —, in opal glass, V. 501c  
 —, mineral, III. 440b  
 —, ore, I. 264c  
**Cryolithionite**, I. 286b; III. 441a  
**Cryoscopy**, III. 441b  
 —, Beckmann, III. 442a  
 —, micro-Rast, III. 443c  
 —, precision methods, III. 444b  
 —, values of K, III. 441c  
**Cryptal**, III. 445c  
**Cryptolite**, II. 512b  
**Cryptopine**, III. 445c  
**alloCryptopine**,  $\alpha$ - and  $\beta$ -, II. 528a, 529a  
**Cryptopyrrole**, I. 601d  
 —, carboxylic acid, I. 601d  
**Cryptotaenene**, III. 445c  
**Cryptotaenia japonica**, III. 445d  
**Cryptoxanthin**, see Kryptoxanthin.  
**Crystal growth**, III. 446a, 454b  
 —, velocity, III. 454b  
**Crystallisation**, III. 445d  
 —, by cooling, III. 448b  
**Crystalliser**, cooling, III. 418b  
 —, —, Howard, III. 451a  
 —, —, pan or tank, III. 448b  
 —, —, Passburg, III. 449a  
 —, —, Swenson-Walker, III. 450a  
 —, —, Wulff-Block, III. 450b  
 —, evaporator, III. 451c  
 —, —, Borske Saltwerker, III. 452b  
 —, —, Jeremiasen or Oslo, III. 452d  
 —, —, pan or tank, III. 451c  
 —, —, salting, III. 451d  
 —, vacuum, III. 453b  
 —, —, rocker type, III. 453d  
**Crystallisers**, crystallisation in, III. 453b  
**Crystallizing plants**, III. 448a  
**Crystalloids**, III. 270a  
**Crystalloluminescence**, III. 22d, 23d  
**Crystals** of marketable sizes, III. 448a  
 "Crystolon," I. 4a; II. 361b  
**Cubanite**, III. 455a  
**Cubebol**, III. 455b  
**Cubebs**, essential oil, II. 188d  
 III. 455c  
**Cuckoo-pint**, I. 497d  
**Cucumber**, III. 455c  
**Cucumis sativus**, III. 455c  
**Cudbear**, III. 456a  
**Cullen earth**, III. 456a  
**Cullet**, V. 673d  
**Cullinan diamond**, III. 578a  
**Culmorin**, V. 56d  
**Cumar** resin in lacquers, II. 472b  
**pseudoCumene**, I. 460d; III. 457a  
**Cumenes**, III. 456a  
**Cumidine** or 4-isopropylaniline, III. 457d  
**o-Cumidine**, III. 457d  
**pseudoCumidine** or 2:4:5-trimethylamine, III. 458a  
**Cumidines**, III. 457d  
**Cuminol** in camphor oil, II. 249c  
**Cummin** or **cumin**, III. 458b  
 —, oil, III. 458d  
**Cupferron**, analytical reagent, II. 583b; III. 335b, 459a  
 —, prepn., VI. 404b  
**Cuprammonia silk**, see Cuprammonium rayon.  
**Cuprammonium rayon**, II. 403b; III. 355a; V. 113a, 116a

- Cuprammonium** silk, *see* Cuprammonium rayon.  
**"Cuprase,"** III. 459a  
**Cuprea** bark, III. 160d  
 **$\beta$ -isoCupreidine,** III. 170d  
**Cupreine,** III. 128a, 160d  
**isoCupreine,**  $\alpha$ - and  $\beta$ -, III. 176b, d  
**Cuprene,** I. 80a, 87a  
 — in respirators, III. 19d  
**"Cupretenin8,"** III. 178b  
**Cupri-adeptol,** III. 459a  
**Cupric bromide,** III. 357a  
 — chloride, III. 356d  
 — compounds, *see also* Copper compounds.  
 — ferrocyanide, III. 470d  
 — fluoride, III. 357b  
 — hydroxide, III. 351c  
 — nitrate, III. 358d  
 — nitrite, III. 358c  
 — oxide, III. 351b  
   phosphate, III. 359a  
   phosphide, III. 355c  
 — salts, III. 356d  
 — —, qualitative reactions, II. 551c, 566d  
 — — —, rare metals present, II. 554d, 556d  
 — sulphate (*see also* Copper sulphate; Copper vitriol), III. 357b; VI. 298a  
 — —, native, II. 517a; III. 341c  
   sulphide, III. 355b  
**Cuprite,** II. 518a; III. 341c, 459a  
**Cuprodesclowitzite,** III. 560b  
**"Cuprol,"** III. 459a  
**Cupron,** II. 605d; III. 459b  
**Cuprosilicon,** III. 355c  
**Cuprous acetylide,** II. 280d  
 — bromide, III. 356c  
 — chloride, III. 356a  
 — compounds, III. 356a  
 — cyanide, III. 356d  
 — ferrocyanide, III. 171b  
 — fluoride, III. 356c  
 — hydroxide, III. 351a  
 — iodide, III. 356c  
 — lactate, ammoniacal, absorbent of carbon monoxide, II. 345b  
 — oxide, III. 353d  
 — —, native, II. 518a  
   phosphide, III. 355b  
 — salts, III. 356a  
 — —, ammoniacal, absorption of carbon monoxide in, II. 345b  
 — —, qualitative reactions, II. 566c  
   sulphate, III. 356d  
   sulphide, III. 355a  
 — —, native, III. 517d  
 — sulphite, III. 356d  
 — thiocyanate, III. 356d  
**Cuprum lazareum,** I. 583d  
**Curacit-soda,** III. 459b  
**Curare,** III. 459b  
 —, calabash or gourd, III. 160a  
 —, para, III. 459d  
 —, pot, III. 460b  
 —, tubo-, III. 459d  
**Curarine,** III. 460a  
**Curcas oil,** III. 460c  
**Curcine,** III. 461b  
**Curcinoic acid,** III. 461a  
**Curcubita pepo,** I. 459b  
**Curcuma aromatica,** III. 461b  
**Curcumenes,** III. 461b  
**Curcumin and Curcuma spp.,** III. 461c  
**Curd,** II. 160d  
**Curine,** III. 459d  
**Curite,** III. 461c; VI. 155a  
**Curran,** black, red and white, III. 461c  
**Currying,** III. 551b  
**Curtius** degradation of azides, I. 308d; II. 375a  
**Cuscaminine,** III. 128b, 161c  
**Cuscamine,** III. 128b, 161c  
**Cusco bark,** III. 161c  
**Cuscohygrine,** III. 226a  
**Cusconidine,** III. 128b, 161d  
**Cusconine,** III. 128a, 161d  
**Cuspareine,** III. 162d  
**Cusparia** bark, cusparine, galipune and minor alkaloids, III. 462b  
**Cusso,** III. 463c  
**Cutch,** I. 11c; R. 433b  
**Cutocellulose,** II. 167a  
**Cutting oils,** IV. 303d  
**Cyameliide,** III. 506d  
**Cyanamide and its detn.,** III. 505a, 511a  
**Cyananthrene,** I. 121c  
**Cyananthrol,** I. 232b  
 — R (B, 1900), I. 106a  
**Cyanase,** IV. 282d  
**Cyanate,** detn., volumetric, II. 651c; III. 511b  
**Cyanates,** prepn., III. 506b, 507a  
 —, qualitative reactions, II. 506b; III. 510b  
**Cyanenin,** III. 511b  
**Cyanhydrins,** I. 195b  
**Cyanic acid,** III. 506d  
**"Cyanicides,"** VI. 101d  
**Cyanidation** or cyanide process of gold extraction, *see* Gold extraction, cyanide process.  
**Cyanides,** III. 463c  
 —, alkali analysis, III. 510b  
 —, —, from ammonia and alkali carbonates, III. 479a  
 —, —, —, alkali metals and carbon, III. 179d  
 —, —, —, ferrocyanides, III. 478c  
 —, —, —, hydrocyanic acid, III. 480d  
 —, —, —, nitrogen, alkali metals and carbon, III. 483c  
 —, —, —, and alkali metal carbonates, III. 481d  
 —, —, —, thiocyanates, III. 480c  
 —, alkali earth, from carbides and nitrogen, III. 487d  
 —, —, —, carbonates, carbon and nitrogen, III. 490a  
 —, —, —, cyanamide and carbon, III. 488c  
 —, —, —, hydrocyanic acid, III. 491b  
**isoCyanides,** alkyl, I. 309a; IV. 359d  
**Cyanides,** complex iron, III. 465a  
 —, detn., potentiometric, II. 706a  
 —, —, volumetric, II. 654d; III. 510b  
 —, drop reaction, II. 582a  
 —, heavy metal, III. 485d  
**Cyanides,** history, III. 463c  
 —, qualitative reactions, II. 569b, 582a, 683c; III. 509c  
**Cyanide** solutions from noble metal extraction, analysis, I. 531d  
**Cyanidin,** I. 381c; III. 512b  
 — chloride, colour base and pseudo-base, III. 512c, d  
 — glucosides, III. 115d, 512c  
 — pigments, flowers containing, III. 512b, 513d  
 —, reduction to *dl*-epicatechin, II. 437c  
 —, relation to callistephin, II. 234d  
**perCyanilic acid,** V. 386c  
**Cyanin,** I. 381b; III. 513d  
**Cyanine** dyes, III. 514c  
 — quaternary bases, III. 523a  
**Cyanines,** 2,1'- and 4,1'-, III. 520d  
 — 2,2'-, 2,4'- and 4,1'-, III. 515a  
**apoCyanines,** III. 529a  
**isoCyanines,** III. 515a  
**neoCyanines,** III. 529c  
 **$\psi$ -Cyanines,** III. 515a, 516c  
**Cyanines,** definition, III. 530d  
 — indotriarbo-, III. 527b  
 — nomenclature, III. 530d  
 — oxacarbo-, oxa-2', and oxa-1', III. 520b  
 — seleno-1', III. 520d  
 — substituted in the chain, III. 524c  
 —, thia-1', III. 520d  
 — thiazinolo-, thiazolocarbo-, thiazolo-, thiazolo-1', thiazolo-2', and thiazolo-4', III. 521b  
 — thiazolocarbo-, thiazolino-2', and thiazolino-4', III. 521d  
**Cyanite,** I. 261d, 370b  
**Cyanoacetic ester,** condensation with aldehydes, II. 360a  
**Cyanoaurate,** potassium, III. 486a, VI. 115d  
**Cyanocamphor,** II. 241c  
**Cyanocarvomenthones,** II. 408c  
**Cyano-compounds,** synthesis, II. 361d, 369c  
**Cyanogen,** III. 503b  
 — bromide and chloride, III. 11b, 504c  
 — — in warfare, III. 10c  
 —, detection of, gaseous, II. 569a, 683c  
 —, detn. of gaseous, II. 683c; III. 504a  
**Cyanoguanidine,** III. 602d  
**Cyanomacurin,** I. 497d; II. 531b  
**Cyanophoric glycosides** (*see also* Amygdalin; Emulsin), III. 531b  
**Cyanuric acid and ethyl ester,** III. 506d; IV. 360d  
**isoCyanuric acid and ethyl ester,** V. 385d; IV. 301a  
**Cyanuric triazide,** I. 563c  
**Cyclamen europaeum,** III. 531c; VI. 87a  
**Cyclamin,** III. 531c, 554c  
**Cyclamiretin,** III. 531c  
**apoCyclene,** III. 531c  
**Cyclenes** (cyclic olefins), III. 532a  
 —, mono-olefinic, III. 532a

- Cyclic dienes**, conjugated, III.  
534b  
-- polyenes, conjugated, III.  
534b  
"Cycloform," I. 369b; III.  
535d  
**Cyclonite**, III. 535d  
**cyclo Paraffins** in petroleum,  
III. 537b  
**cyclopentadiene**, III. 533c  
**Cyclopterine**, I. 459c  
"Cycloran E," III. 537d  
**Cyder**, see Cider.  
**Cygnine**, III. 537d  
**Cylindrite**, III. 537d  
**Cymarin**, III. 385b; III. 538a  
*allo*Cymarin, II. 381c, 385d  
**Cymarine**, enzymic isomerisa-  
tion, III. 381c  
**Cymarose**, II. 300b; 381d;  
III. 538b  
**Cymbopogon martini**, V. 517a,  
518b, 530a  
**Cymene**, dihydroxy-, II. 104c  
-- in essential oils, II. 111a;  
III. 21d, 183b  
**p-Cymene** from camphor, II.  
212c  
-- -- cedrene, II. 410b  
**Cymenes**, III. 538b  
**Cymols**, III. 538b  
**Cymophane**, III. 119a  
*Cynips gallic tinctoria*, V. 425a  
**Cynodontin**, V. 55a  
**Cynthiaxonanthin**, II. 401d; III.  
539c  
**Cyperene**, cyperol and  
cyperone, III. 120a, 539c  
**Cypress** camphor, II. 441a  
**Cyprian** vitriol (see also Cop-  
per vitriol), III. 537b, 539d  
**Cyrtolite**, III. 539d  
**Cystamine**, I. 326a  
"Cystazol," III. 540a  
**Cysteic acid**, III. 511b  
**Cysteine**, III. 540c, 541a  
-- and cystine, detn., III. 541c  
**Cystine**, III. 540a  
**Cystogen**, I. 326a  
"Cystopurin," III. 542b  
**Cytase**, II. 87d; III. 542b  
**Cytidine**, VI. 87a  
**Cytisine**, I. 619c; III. 542c,  
544a  
**Cytisolidine**, III. 543a  
**Cytisoline**, III. 513a  
**Cytochrome**, III. 544a; IV.  
311b; VI. 105a  
**Cytosine**, III. 545c  
**Cytromycetin**, V. 53d
- D**
- δ-Acid** (delta acid), III. 557b  
*Daemonorops propinquus*, IV.  
55d  
**Dahlia**, co-pigmentation in, III.  
341b  
**Dahl's acids**, III. 545b  
**Daidzein**, V. 259c  
**Daidzin**, V. 259c; VI. 87b, 88c  
**Dalton's law** of partial pres-  
sures, IV. 35a, 48b  
**Damascenine**, III. 545b  
**Dambonitol**, III. 546a  
**Dambosse**, VI. 495a  
**Dammur** in lacquers, II. 409d  
-- resin, III. 546a  
**Danalite**, III. 547a  
**Dandelion**, III. 547a  
*Daniella thurifera*, III. 338b  
**Dant** in coal, V. 350d  
*Daphnandra* spp. and alkaloids,  
III. 547b  
**Daphnandrine**, III. 547b  
*Daphne* spp., III. 547d  
**Daphnetin** and daphnetinic  
acid, III. 547d  
**Daphnin**, III. 413a, 547d, 548b  
**Daphnoline**, III. 547c  
**Darak**, II. 408c  
**D'Arcet's alloy**, I. 698c  
"Darco," I. 153a  
**Dari**, II. 182c  
**Darwinite**, III. 548c; IV. 55b  
**Date**, III. 548c  
**Datile**, III. 549a  
*Datisca cannabina*, I. 199a;  
III. 549a  
**Datisectin** and datiscin, III.  
549a, c  
**Datiscin**, rutinose in, II. 300c  
**Datolite**, II. 229d; III. 549d  
*Datura stramonium* and datu-  
rine, III. 550a  
**Daucol**, II. 401b  
**Daucusin**, II. 101b  
**Dauerhefe**, V. 15a  
**Dauricine**, III. 550a  
**Dautriche** test of explosives,  
IV. 550d  
"Davidamon," III. 550b  
**Dawsonite**, I. 264d  
**Deacon** chambers in bleaching  
powder production, III.  
61a  
process, II. 128c; III. 41b,  
48b  
**Dead dipping** of brasswork, III.  
550b  
**Deadly nightshade**, I. 603b  
**Dead oil** from shale, III. 550c  
**Debye-Hückel** limiting law,  
VI. 246a  
**Decacyclene**, III. 550c  
**Decaethylene glycol**, IV. 379b  
**Decahydronaphthalene**, see  
Decalin.  
**Decahydroretene** carboxylic  
acid, dmitro-, I. 3b  
**Decalin** (decaline), III. 426d;  
VI. 352c  
**Decalols**,  $\alpha$ - and  $\beta$ -, VI. 354b  
**Decamethylene** dicarboxylic  
acid, III. 550d  
**Decan grass**, II. 482d  
**Decenylene acid**, II. 272c  
**Dechenite**, III. 551a  
"Decholin," III. 551a  
*n-Decoic acid*, II. 271b  
**Decyl acetate**, III. 551b  
-- alcohol, III. 551b  
-- aldehyde, III. 551b  
**De-emulsification**, IV. 300b  
**Defibrination** of blood, II. 24b  
**Deficiency diseases**, see Ash;  
Calcium gluconate; Ferti-  
liser, borax, remedial.  
"Degalol," III. 551b  
**Dégras**, III. 551b, 551d, foot-  
note; VI. 135c  
**Dégrasbildner**, dégras-former,  
III. 552b  
**Deguelin**, III. 550c  
**Degumming** benzol with silica  
gel, III. 267d  
-- silk, II. 17b; IV. 143d  
**Dehumidification**, VI. 286d  
**Dehydracetic acid**, I. 63d  
**Dehydrase**, III. 553a  
**Dehydrating agents** in organic  
prepn., IV. 350b  
**Dehydration** (see also Drying),  
IV. 58a  
-- , azeotropic distillation  
method (see also Distilla-  
tion, laboratory), I. 103c,  
178c  
-- , catalytic, II. 428a  
*trans-Dehydroandrosterone*,  
VI. 275a  
**Dehydrocarveole**, dehydrocar-  
vone, II. 278b  
**7-Dehydrocholesterol**, II.  
203a  
**Dehydrocinchonine**, III. 139c  
**Dehydrocorticosterone**, VI.  
277b  
**Dehydrocorydaline**, III. 401a  
**Dehydrodieugenol**, IV. 390b  
**Dehydrodi-isoeugenol**, IV.  
390c  
**1:5-Dehydro-5:5'-dihydantyl**,  
VI. 289d  
**Dehydrogenases**, III. 553a;  
IV. 315b  
-- in muscle extract, VI. 78c  
**Dehydroindigotin**, VI. 452d  
**Dehydronorcaryophyllenic**  
acid, II. 409d  
**Dehydronorcholene**, carcin-  
ogenic compound from, II.  
379d  
**Dehydroquinine**, III. 139c  
**7-Dehydrositosterol**, II. 203a  
**Dehydrothio-m-xylylidine**, III.  
553c  
**Dehydrotriacetonamine**, I.  
68d  
**Dekaborane**, II. 40d  
**Dekol**, III. 553d  
"Dekrysil," III. 553d  
**Dolatzenite**, I. 302d  
**Delcosine**, III. 557a  
**Delphin**, III. 553d  
**Delphinidin**, I. 381c; III.  
553d, 554c  
-- , relation to callistephin, II.  
234d  
**Delphinin** (glucoside), III.  
555c  
**Delphinine** (alkaloid), II.  
556c, 557a  
*Delphinium consolida*, III.  
555c, d  
-- spp., alkaloids, III. 556c  
-- *zaili*, D. spp., dyeing proper-  
ties, I. 499a; III. 555d  
**Delphinoidine**, III. 557b  
**Delphisine**, III. 557a  
**Delphocurarine**, III. 556c  
**Delsoaline**, III. 557a  
**Delta acid** ( $\delta$ -acid), III. 557b  
**Delustring** processes, V. 202a  
**Demantoid**, V. 429c  
**Demargarinated oil**, III. 410d  
**Denaturants**, III. 557a  
**Dendrites**, I. 164a  
**Denier** count of rayon, IV.  
125a; V. 112d, foot-note.  
**Densimeter**, III. 558c  
**Dentifrices**, perborates in, II.  
52a  
**Deodorants**, perborates in, II.  
52a  
**De-oiling** processes for emul-  
sions, IV. 300b  
**Deoxyadenosine**, VI. 87c



- Deoxyalizarin**, 1. 219c  
**Deoxyamalic acid**, VI. 407c  
**Deoxycholic acid**, 1. 689b  
 —, carcinogenic compound from, II. 379d  
 —, compound with camphor, II. 188c  
**Deoxycorticosterone**, VI. 278b  
**Deoxycytidine**, VI. 87c  
**Deoxyguanosine**, VI. 87c  
**Deoxysantalol**, 1. 650c  
**Deoxysantalol**, II. 260d  
 —, acetyl-, II. 260d  
**Deoxyuridine**, VI. 87c  
**Dephlegmator**, III. 558d  
**Depressants** (flotation process), V. 263d, 266a  
 "Dericinoel," II. 422b  
 "Dermatol," 1. 700d; III. 558d  
 "Dermogene," III. 559a  
 "Dermol," 1. 701a; III. 117d, 559a  
**Derris and D.** resin, III. 559a, c  
 "Desalgin," III. 560a  
**Descloizite**, III. 560b  
**Desiccation**, see Drying.  
 "Desichtol," III. 560b  
**Desoxycinchonidine**, III. 147d, 153d  
**Desoxycinchonine**, III. 147a, 158c  
**Desoxyhydrocinchonidine**, III. 162d  
**Desoxyhydrocinchonine**, III. 164a  
**Desoxyhydroquinidine**, III. 165c, 167b  
**Desoxyquinidine**, III. 172a  
**Desoxyquinine**, III. 177d  
 "Despyrin," III. 560b  
**Dessoulavy compound**, VI. 450c  
**Destearinated oil**, III. 110d  
**Desyl chloride**, 1. 140d  
**Detergents**, II. 427; VI. 509d  
 — from petroleum, III. 560c  
 —, perborates in, II. 52a  
**Detonating fuze**, III. 361b  
**Detonation** (see also Explosions, gaseous), IV. 451c  
 — by "influence," sensitivity of explosives to, IV. 550a  
 — in gaseous explosions, IV. 431c, 436a  
 — of electrolytic gas, effect of diluents, IV. 439d  
 — — explosives, velocity, IV. 550c  
 — —, spin in, IV. 436d  
 — pressures and velocities in gaseous explosions, IV. 440a  
 —, sensitivity of explosives to, IV. 549b  
 — velocity, Dautriche detn., IV. 550d  
**Detonators**, IV. 535c, 544c  
 —, lead plate and nail tests, IV. 545a  
**Detonit**, Wetter, R. IV. 556a  
 "Dettol," III. 560c  
**Deuterium** (heavy hydrogen), III. 560d  
 — as indicator in biology, III. 566b  
 — compounds, III. 505a  
 —, detn., III. 566a  
 —, deuterium hydride and hydrogen, properties compared, III. 563a  
**Deuterium**, heterogeneous interchange reactions, III. 560b  
 —, homogeneous interchange reactions, III. 505d  
 —, interchange reactions, III. 565d  
 — oxide (heavy water), III. 561a  
 — and water, properties compared, III. 561b  
 —, electrolytic concentration, III. 561d  
 —, reactions in, III. 563c  
 —, separation from hydrogen, III. 562b  
 —, spectroscopic data, III. 566c  
**Deuteroporphyrin**, VI. 162d, 163d  
 — in synthesis of hamin, II. 20c  
**Deutsche Leg.**, 215; 1. 277c  
**Devarda's alloy**, II. 598d, 661a; III. 567b  
**Developer O**, IV. 149c  
**Devil liquor**, 1. 318c  
**Devil's cotton**, 1. 4c  
 "Devils Dung," 1. 198a  
**Dewaxing of oils by trichloroethylene**, 1. 103c  
**Dextran**, III. 567c  
**Dextrin formation**, II. 142d  
**Dextrins**, II. 282b; III. 567c  
 —, limit, I and II, III. 568b  
 "Dextrins, stable," III. 569c  
 "Dextroform," III. 571a  
**Dextrose** (glucose, *d*-glucose), II. 282b, 281a, 289a  
 —, relation to cellulose, II. 157a  
**Dhak**, II. 157d  
**Dhurrin**, II. 183d; III. 571a  
**Diabase**, II. 311b; III. 571a  
**Diabetes mellitus**, VI. 141a, 196d  
 "Diabetin," III. 571b  
**Diacetamide**, 1. 60b  
**Diactin**, 1. 60b  
 — as plasticiser, II. 118c  
**Diactenamine**, 1. 68d  
**Diactone alcohol**, 1. 66d  
 —, catalysed decomposition, VI. 252b  
 — in film dopes, II. 448c  
 — lacquers, II. 170b  
 —, specification, II. 172b  
 — cyanohydrin, 1. 68d  
**Diactyl**, 1. 19b; III. 571b  
**Diactyldioxime** (see also Dimethylglyoxime), IV. 5d  
**Diactyl in butter**, II. 103c; V. 306a  
 — food, II. 80c, 198b  
**Diactylenes**, III. 571b  
**Diacidines**, 1. 130b  
**5:5-Diacridyl**, 1. 130b  
**Diacridyl dimethonitrate**, 1. 130c  
 "Dial," 1. 623a; III. 573a  
**Diallage**, III. 573a  
**Diallyl**, II. 156d  
**Diallylaniline**, 1. 257c  
**Diallylbarbituric acid**, 5:5-dibromo-, 1. 623a  
**5:5-Diallylbarbituric acid**, 1. 623a  
**Dialuric acid and derivs.**, 1. 625a  
**isoDialuric acid and derivs.**, 1. 626a, b  
**Diamine dyes**, IV. 219b  
**Diamines**, aliphatic, 1. 314c  
 —, aromatic, 1. 315c  
**Diamond**, II. 300a; III. 573a  
 — as abrasive, 1. 3d; III. 578b  
 "Diamonds," Marmorosch," and "Maturn," V. 514a  
**Diamorphine hydrochloride**, 1. 65d  
**o-Dianisidine**, III. 578c; IV. 12d  
**Dianthracene**, 1. 384d  
**Dianthranol**, 1. 432b  
**Dianthranyl**, 1. 432b  
 —, 2:2-dihydroxy-, 1. 215b  
**1:2'-Dianthraquinonylamine**, 1. 206b  
**Dianthraquinonyls**, 1. 111d  
**Dianthrimides**, 1. 420a  
**Dianthrone**, 1. 432b  
**Diaphorase**, V. 33a, 31b  
 "Diarsenol," III. 578d  
 "Diapsirin," III. 578d  
**Diaspore**, 1. 264c; II. 25c; III. 579a; VI. 101b  
**Diasporite**, III. 579a  
**Diastase** (see also Amylase; Brewing), II. 76b, 298d  
**Diatomaceous earth**, diatomite, III. 579a; IV. 239b  
**1:4-Diazine**, 1. 564b, d  
**Diazoacetate**, ethyl, III. 500a  
**Diazoacetic ester**, catalytic decomposition, VI. 251c  
**Diazoacetone**, III. 600b  
**Diazoamines**, aliphatic - aromatic, III. 590c  
 —, aromatic, III. 595d  
**Diazoaminobenzene**, III. 595d  
**Diazoamino-compounds**, III. 580c  
**Diazoaminomethane**, III. 596d  
**Diazoamino-p-toluene**, III. 590c  
**Diazo-anhydrides**, III. 597d  
 — anthranilic acid, III. 593a  
**Diazobenzene**, see also under Diazo-compounds; Diazonium compounds.  
 — hydrate or hydroxide, III. 590c  
**Diazobenzeneimine**, 1. 581c  
**Diazobenzenesulphonic acid**, 392d; III. 592d  
**Diazocamphor**, II. 245b  
**Diazo-components**, III. 583b, 587b; IV. 159d  
 — compounds (see also under Diazobenzene; Diazonium), III. 580b; IV. 191d  
 —, anti- and syn-, III. 591a  
 —, aliphatic, III. 598a  
 —, cyclic, III. 592d  
 —, light-sensitive, II. 452c; III. 589d  
 —, metallic derivs., III. 597a, 600b  
 —, prepn., II. 429a  
 —, stable, solid or paste, III. 589b; IV. 231c  
 —, stabilised, in photography, III. 588d  
 —, stereochemistry, III. 591a  
 — coupling process, IV. 198d  
**Diazocyanides**, III. 580c, 597d, 598a  
**Diazodinitrophenol**, III. 600c  
**Diazoethane**, III. 600a

- Diazo-group**, miscellaneous substitutions, III. 586d  
 — —, reduction, III. 584d  
 — —, replacement by hydrogen, II. 584d  
 — —, — — sulphur or sulphur-containing radicals, III. 586a  
 — —, — — the cyanate or cyanide radical or by halogen, II. 429a; III. 585a  
 — —, — — nitro- or nitroso-radical, III. 586b  
 — — hydrates, III. 586b  
**Diazohydroxides**, III. 580b  
**Diazoo acids**, aromatic, III. 597d  
**p-Diazoimides**, III. 594c  
**Diazoimines**, cyclic, III. 593b  
 — from *o*-, *p*- and *peri*-diamines, III. 589c, 593b  
**p-Diazoiminobenzene** and derivs., III. 591c  
**Diazomethane**, III. 590b  
**Diazomethanedisulphonic acid**, III. 600b  
**Diazonium** arylsulphinates, III. 581c  
 — aurichlorides, III. 581b  
 — azides, III. 581b  
 — borofluorides, III. 581c  
 — carbonates, III. 581b  
 — chromates, III. 581b  
 — compounds, *see also under* Diazobenzene; Diazo-compounds  
 — —, aromatic, constitution, III. 590b  
 — —, reactions, III. 583b, 587a  
 — —, coloured, III. 591c  
 — —, coupling, III. 587b  
 — —, electrolytic prepn., III. 583a  
 — — from hydrazines, III. 583a  
 — —, interchange of groups in, III. 588a  
 — —, internal, III. 592d  
 — —, non-aromatic, III. 591d  
 — —, isoxazole series, II. 592b  
 — —, pyrazole series, III. 592a  
 — ferricyanides, III. 581b  
 — fluorides, III. 581b  
 — nitrites, III. 581b  
 — nitroprussides, III. 581b  
 — perchlorates, III. 581b  
 — phosphomolybdates, III. 581c  
 — phosphotungstates, III. 581c  
 — picrates, III. 581b  
 — platinumchlorides, III. 581b  
 — plumbichlorides, III. 582c  
 — salts, III. 580b, 582c  
 — stannichlorides, III. 581b  
 — sulphates, III. 592d  
 — thioacetates, III. 581c  
 — thiosulphates, III. 581b  
 — tungstates, III. 581c  
 — zincchlorides, III. 581c  
**Diazo-oxides**, III. 580b  
 — —, aromatic, III. 591a  
 — —, binuclear, III. 597a  
**2-Diazo-phenol**, 4:6-dinitro-, III. 600c  
**Diazo- $\psi$ -semicarbazines**, III. 586d  
**Diazosulphides**, II. 580c  
**Diazosulphonates**, III. 580c  
 —, *syn*- and *anti*-, III. 598c  
**Diazosulphonic acids**, *see* Diazonium sulphonates.  
 — —, potassium salts *syn*- and *anti*-, III. 598d  
**Diazotates**, *syn*- and *anti*-, III. 580b, 591c  
**Diazotisation**, III. 580c  
 —, special methods, IV. 237c  
 —, velocity, III. 582c  
**Diazotising agents**, III. 582c  
**"Diazotype"** photographic paper, III. 590a  
**Diazouracil**, reaction with sucrose, II. 300b  
**Dibabiturylalkylamines**, I. 249b  
**Dibenzanthracene**, carcinogenic action, II. 378d  
**Dibenzanthrones**, I. 414a, 424a  
*iso*Dibenzanthrone, I. 414a  
**Dibenzanthrone vat dyes**, I. 206a  
*oo'*-Dibenzil, III. 600d  
**Dibenzopyrenequinones**, I. 426b  
**Diborane**, II. 40d  
**Diborate**, sodium, *see* Borax.  
**"Dibromin"**, I. 623a; III. 600d  
**Dibromoethane**, *see* Ethylene dibromide.  
**Di-isobutaldehyde**, II. 157b  
**Di-isobutylacetoacetic acid**, ethyl ester, I. 64d  
**Dibutylamines**, II. 170b  
 $\gamma$ -Di-*n*-butylaminopropyl *p*-aminobenzoate, II. 179b  
**Diisobutyl nitrosamine**, II. 176c  
**N:N'-Diisobutyloxamide**, II. 175d  
**Dibutyl phthalate**, specification, II. 472c  
**Dibutylalidine**, II. 157a  
**Dibutyl peroxide**, II. 180a  
**Dicarbazyls**, II. 279a  
**Dicarbocyanines**, *s*- and *as*-, III. 520a  
**Dicarboxylic acids**, III. 600d  
 $\alpha$ -Dicarvelone, II. 107b  
*Dicentra spp.*, III. 601b; VI. 1a  
**Dicentrine**, III. 601b  
**Dichloramine T**, III. 36b, 601d  
**2:5-Dichloroaniline**, III. 601d  
**Dichloroethylene**, I. 104a  
 $\alpha\alpha'$ -Dichlorohydrin, VI. 67d  
**Dichlorohydrin** in lacquers, II. 478d  
**Dichroite**, III. 602a  
**Dichromates**, reactions and detn., *see* Chromates; Chromium.  
**Dichromated gelatin**, *see* Gelatin, bichromated.  
**Dicinchonine**, III. 161d  
**Dicinchonine**, III. 128a, 161d  
**Diapocinchonine**, III. 162a  
**Dictroneloxide**, III. 191a  
**"Di-citurin"**, III. 602a  
**Dickite**, III. 196a, 602a  
**Diconquinine**, III. 128b, 162a  
**Dicresylin** in lacquers, II. 478d  
**Dicrotyl**, II. 150d  
**Diisocrotyl**, II. 156d  
**Dictamine**, III. 602b  
**Dictamnolactone**, III. 602c  
**Dicyanane**, III. 517d  
 $\psi$ -Dicyananes, III. 516d  
**Dicyanodiamide**, III. 602d  
**Dicycmena**, III. 530a  
**"Didial"**, III. 603c  
**Didymium** in cerite, II. 507a  
**Dieckmann reaction**, II. 366d  
**Diels-Alder reaction**, II. 152d  
**Dielectric constant**, II. 709b  
**Diene reaction of fatty oils**, IV. 82b  
 — synthesis, I. 208a  
**"Dienu"**, IV. 87a  
**Diesel oil**, III. 423d  
 — fuel production, II. 425d  
**Diethylacetic acid**, II. 271c  
**Diethylaniline**, III. 603d  
**Diethylacetoacetic acid**, ethyl ester, I. 64d  
**Diethylamine**, IV. 355a  
 —,  $\beta\beta$ -diamino-, IV. 376d  
 — from acetylene, I. 84c  
**Diethyl-*m*-aminophenol**, III. 603d  
**Diethylcarbinol**, I. 359d  
**Diethyl carbonate** in lacquers, II. 470b  
 — catechol ether, II. 431b  
**Diethylchloroamine**, IV. 355b  
**Diethyl compounds**, *see also under* Ether; Ethyl.  
 — cyanurate, IV. 361a  
 — isocyanurate, IV. 361b  
**Diethylcyanuric acid**, IV. 361a  
**Diethylisocyanuric acid**, IV. 361b  
**Diethyldiphenylurea**, II. 480c  
**Diethylene bromohydrin**, IV. 379a  
 — chlorohydrin, IV. 378d  
**Diethylenediamine**, IV. 376c  
**Diethylene dihydrate**, IV. 379a  
 — dioxide, IV. 380c  
 — disulphide, IV. 380d  
 — glycol, IV. 378d  
 — monoethyl ether, II. 282a  
**"Diethylene triamine"**, IV. 376d  
**Diethyl ether**,  $\beta\beta$ -dihydroxy-, IV. 378d  
*as*-Diethylhydrazine, IV. 362b  
*s*-Diethylhydrazine, IV. 362c  
**Diethylhydroxylamine**,  $\alpha\beta$ - and  $\beta\beta$ -, IV. 363a  
**Diethyldiene hydrazine**, IV. 382a  
**Diethylmethacetic acid**, VI. 205c  
**Diethylnitroamine**, IV. 355b  
**Diethylisnitroamine**, IV. 355c  
**Diethylnitrosoamine**, IV. 355c  
**Diethyl orthophosphate**, IV. 366c  
 — peroxide, IV. 366b  
 — phosphite, IV. 367a  
**Diethylphosphoric acid**, IV. 366c  
**Diethyl phthalate**, specification, II. 472c  
 — pyrophosphate, IV. 366d  
**Diethylpyrophosphorous acid**, IV. 367b  
**Diethyl selenate**, IV. 367c  
 — selenite, IV. 367d  
**"Diethylstilbestrol"**, VI. 272b  
**Diethyl sulphate**, IV. 368d  
 — sulphide, IV. 370a  
 —,  $\beta\beta$ -dichloro-, in gas warfare, III. 8c, 11b  
 — —, prepn., detection and detn., IV. 371a

- Diethyl sulphine oxide**, IV. 370b  
 — sulphite, IV. 309b  
**Dietzeite**, III. 604a  
**Di-isoeugenol**, IV. 309c  
**Difference** figure of m.p. of fats and fatty acids, II. 185b  
**Diffraction** method of determining interatomic distances, VI. 502c  
**Diffusion**, III. 604b  
 —, anomalous, III. 607b  
 — batteries, IV. 566b  
 — coefficients in mol. wt. detn., III. 606d  
 — of gases through metals, III. 605b; VI. 331d  
 — liquids and solutes, III. 600a  
 — — solids, III. 607c  
**Diffusivity**, thermal, V. 545b  
**Diflavone**, V. 258b  
**Diflavanol**, V. 262a  
**Digalacturonic acid** in apple pectin, II. 298a  
**m-Digallic acid**, IV. 1a; V. 424d  
**p-Digallic acid**, IV. 1a  
**Digermane**, V. 522a  
**Digesters**, VI. 24a  
**Diglanides** A, B and C, II. 385a  
**Diginin**, II. 384a  
**Digitalin**, II. 384d  
**Digitaline** cristallisée (Dige-toxin), II. 381a  
**Digitalis glycosides**, II. 383d  
**Digitalis purpurea**, *D. spp.*, II. 381b, 385a; VI. 88d, 97a  
**Digitalose**, II. 288d, 381d; IV. 1a  
**Digitogenin**, VI. 87d  
**Digitonin**, II. 381a; VI. 87c  
 — test for sterols in butter, II. 160d  
**Digitoxigenin**, II. 382a, 381b  
**Digitoxin**, II. 381a  
**Digitoxose**, II. 288b, 381c, 381b; IV. 1b  
**Diglycerin**, VI. 70c  
**Diglyceryl ether**, VI. 70c  
**Digoxigenin**, II. 382a  
**Digoxin**, II. 385a  
**Diheptylacetooacetic acid**, ethyl ester, I. 61d  
**Dihydroacridine**, I. 125d  
**Dihydroanthranol**, I. 132a  
**Dihydrobrazilinic acid**, II. 70a  
**Dihydrocarveol**, II. 405c, 407b, IV. 1b  
 —, reduction, II. 405c  
*neo*-**Dihydrocarveol**, IV. 2a  
**Dihydrocarvone**, IV. 2a  
**Dihydrocarvylamine**, IV. 1c  
**Dihydrocedrene**, II. 440d  
**Dihydrocholesterol**, III. 89b  
**Dihydrocinchonidine**, III. 162b  
**Dihydrocinchonine**, III. 162d  
 —,  $\alpha$ -chloro-, III. 155d  
**Dihydrocinchotoxine**, III. 163c  
**Dihydrocitrinellal**, III. 191d  
**Dihydrocodeinone**, hydroxy-, hydrochloride, IV. 392b  
**Dihydrocodeinone**, III. 324a  
**Dihydrodianthrone**, I. 432b  
**Dihydroeremophilone**, hydroxy-, IV. 324a  
**Dihydroergosterol**, 22:23-, II. 203a  
**Dihydroerethole**, II. 199d  
**Dihydroeucarveol**, IV. 391c  
**Dihydroeucarvone**, IV. 391d  
**Dihydroeugenol**, IV. 390b  
**Dihydroflavone**, II. 519a  
**Dihydroguaicol**, VI. 142b  
**Dihydrohexaborane**, I. 10d  
**Dihydrohumulene**, amino-, II. 109a  
**Dihydroionone**, III. 192a  
**Dihydropseudoionone**, III. 192a  
 $\alpha\beta$ -**Dihydroionone**, IV. 391a  
**Dihydromorphinone** hydrochloride, IV. 4c  
**Dihydropentaborane**, II. 10d  
**Dihydrositosterol** in bran, II. 60b  
 — — rice, II. 493d  
**Dihydro- $\alpha$ -terpineol**, IV. 3a  
**Dihydrotetraborane**, II. 40d  
**Dihydrothujaketone**, IV. 326b  
**2,6-Di-iodophenol**, VI. 267c  
 — "Dika bread," IV. 1a  
**p-Diketocamphane**, II. 212c, 217b  
 — reduction, II. 216a  
 $\alpha\beta$ -**Diketohydrindene**, VI. 300b  
 $\alpha\gamma$ -**Diketohydrindene**, VI. 306c  
**Diketopiperazines**, I. 321b; VI. 73a  
**Dilatometer**, IV. 4b  
 — "Dilaudid," IV. 4c  
 — "Dilecto," IV. 4c  
**Diluturic acid**, I. 627a  
 —, methyl-, and dimethyl-, I. 627d, 628a  
**Dill**, IV. 4c  
 — oil, I. 371c; IV. 5a  
 —, carvone m., II. 106b  
 — "Dimedon," I. 181a; IV. 5a; V. 298a  
**Dimethyl** (see also Ethane), IV. 363b  
**Dimethylacetoacetic acid**, ethyl ester, I. 64d  
**3,4 - Dimethylacetophenone** from camphor, II. 212d  
**3,7 - Dimethylacridine**, 2:8-diamino-, hydrochloride, I. 131c  
**Dimethylacridine**, dihydroxy-, I. 125a  
**2:8 - Dimethylacridinium chloride** (proflavine), I. 134a  
**Dimethylacridinium nitrate**, luminescence, III. 23d  
*as*-**Dimethylallene**, I. 240c  
*s*-**Dimethylallene**, I. 240c  
**Dimethyl - m - aminocresol**, Capri Blue from, II. 271b  
**Dimethylaniline**, IV. 5b  
 —, *p*-nitroso-, II. 271b  
**Dimethylantraquinones**, 1:2-, 1:3-, 1:4-, and 2:3-, syntheses, I. 402c  
**3:3'-Dimethylbenzidine**, IV. 12d  
**Dimethylbenzylcarbinol**, IV. 5c  
**Dimethylbutadiene**, II. 155a  
 $\alpha\beta$ -**Dimethylbutyric acid**, II. 271d  
**Dimethyldiacetonamine**, I. 60a  
**NN - Dimethyldiacridylum salts**, I. 130c  
**5:5 - Dimethyldihydroresorcinol**, see "Dimedon."  
**Dimethyldiketopiperazine**, I. 171a  
**3:3' - Dimethyldiphenylmethane**, 1:4 - dimethyldiamino-, IV. 5d  
**Dimethyldiphenylurea**, II. 180d  
**Dimethylethylacetic acid**, II. 271d  
**1:2 - Dimethyl - 4 - ethylbenzene** from camphor, II. 212d  
*as*-**Dimethylethylene**, II. 177c  
*s*-**Dimethylethylene**, II. 177b  
**Dimethylethylenediamine**, II. 178b  
*s*-**Dimethylethylene oxide**, II. 179b  
**Dimethylglyoxime**, IV. 5d  
 — reagent for nickel, II. 578b, 612c, 672b; IV. 6b  
 — — other metals, IV. 6b  
**5:5-Dimethylhydantoin**, VI. 292c  
**Dimethylhydroquinone**, IV. 6d  
**1:3-Dimethylindole**, 5-hydroxy-, II. 199c  
**Dimethyl ketone**, I. 65d  
**Dimethylmethoxyphenol**, IV. 7a  
**Dimethylparabanic acid**, III. 92d  
**3:7 - Dimethyl - 5 - phenyl - acridine** hydrochloride, 2:8-diamino, I. 132b  
**Dimethylphenylpyrazolone** mercury sulphaminate, I. 465d  
 $\alpha\alpha$ -**Dimethylpropionic acid**, II. 271d  
**Dimethylstibine** bromide and chloride, I. 431d  
 — cyanide, I. 434d  
 — oxide, I. 431d  
**Dimethylstibinic acid**, I. 434d  
**Dimethyl succinonitrile**, II. 178b  
 — sulphate in chemical warfare, III. 10c  
 — —, prepn., III. 11c  
**Dimethyltriazenes**, III. 596d  
**Dimethylxanthine**, 1:3- and 3:7-, II. 197d, c  
 — "Dimol," IV. 7a  
**Dinaphthazines**, I. 567c  
**Dinitroanthraquinones**, I. 391a  
**Dinitrobenzenes**, I. 673a, 677a  
**Dinitrochlorohydrin**, IV. 7a, 242c  
**Dinitroglycerin**, IV. 491a  
**Dinitroglycol**, IV. 379d, 489d  
 — "Diocaine," IV. 7b  
**Diocetylacetoacetate**, ethyl, I. 65a  
 — "Diiform," IV. 7b  
 — "Diogen," IV. 7c  
 — "Diogenal," IV. 7c  
**Diolefines** from acetylene, I. 85b  
 — "Dionin," IV. 7c  
**Diopside**, III. 573a; IV. 7c  
**Diopside**, III. 341c, 355d; IV. 7c

- Diorite**, II. 314b; III. 571a; IV. 7d
- Dioscorine**, IV. 8b
- Diosmetin**, IV. 8c
- Diosmin**, IV. 8c; VI. 87b
- Diosphenol**, II. 120c; IV. 8c  
—, formation, II. 404d
- Dioxan**, IV. 380c  
— in lacquers, II. 478d
- Dioxine**, IV. 10a
- Dioxorea spp.**, IV. 10a
- Dioxyconessine**, III. 324a
- Dipentene** by-product, II. 250c  
— from carene, II. 388d  
—, occurrence, III. 183c  
—, nitroso-, II. 407b
- Dipeptidase** in brewing, II. 88c
- "Diphenal,"** IV. 10a
- Diphenanthrazine**, I. 565d
- Diphenazine**, I. 564d, 565d, 567a
- Diphenols** from phenol, II. 305a, 307a
- Diphenyl**, IV. 10a
- Diphenylamine**, IV. 13a  
—, *p*-amino-, IV. 14d  
—, arsenic chloride, III. 11c  
—, as stabiliser, IV. 520c  
—, chloroarsine, in warfare, III. 9a  
—, colour reactions, IV. 14b  
—, detn., IV. 533a  
—, 2,4-dinitro-4'-hydroxy-, IV. 7b  
— from phenol, II. 307a  
— hexanitro- (*s*-hexanitro-), I. 549c; IV. 14d, 489a  
—, 1- and 4-nitro-, IV. 14c  
—, pyrolysis, II. 278c  
— sulphonic acid, Ba salt, as indicator, VI. 430b
- D phenyl**, amino-derivs., IV. 11c  
—, 2-amino-, pyrolysis, II. 278c  
— as heat transfer agent, II. 305b  
— bisdiazonium chloride, III. 582a
- Diphenylchloroarsine**, II. 25b; III. 11c  
— in warfare, III. 8c, 11c
- Diphenylcyanoarsine** in chemical warfare, III. 9d  
—, prepn., III. 11c
- Diphenyl**, 2,2'-diamino-, carbazole from, II. 278c  
—, diaminohydroxy-, IV. 10a
- Diphenyldimethylolid** group, IV. 14d
- Diphenylenemethane**, IV. 15b
- Diphenyl ether** from phenol, II. 305a
- Diphenylhydrazine**, VI. 301c
- Diphenyl**, hydroxy-, from phenol, II. 305b
- Diphenylmethane**, IV. 15b  
—, 4,4'-dimethyldiamino-3,3'-dimethyl-, IV. 5d
- Diphenylmethanedimethyl-dihydrazine**, II. 203c
- Diphenylmethane** perfume, V. 519a
- Diphenylmethylolid**, penta-hydroxy-, IV. 277d
- Diphenyl**, octahydroxy-, II. 195a
- Diphenyl oxide**, IV. 16c
- Diphenyl oxide**, as heat transfer agent, II. 305b  
—, perfume, V. 519a  
— phthalate in lacquers, II. 472c
- Diphenylpolyenes**, II. 398b
- Diphenyls**, chloro-, as heat transfer agents, IV. 10c, 11a
- Diphenylstibine chloride**, I. 433c
- Diphenyl sulphide**, hexanitro-, IV. 484c
- Diphenylsulphone**, hexanitro-, IV. 484d
- as-Diphenylurea**, I. 172a; IV. 14d
- Diphosgene** in chemical warfare, III. 8b
- 1:3-Diphosphoglyceric acid**, VI. 78a
- "Diplosal,"** IV. 16c
- Dippel's oil**, I. 327d; II. 29c
- "Dipropesin,"** IV. 16d
- Di-isopropenyl**, II. 155c
- Dipropylacetal**, IV. 382d
- Dipropylacetoacetic acid**, ethyl ester, I. 64d
- Dipropyl ketone**, II. 181d
- Dipterocarpus spp.**, VI. 156c
- Dipy**, III. 328c
- Diquinicine**, III. 162a
- Diquinine carbonate**, I. 460b
- Disaccharides** (*see also* Glycosides), II. 298b
- Disacryl**, I. 136b
- "Disalol,"** IV. 16d
- Disazo-acid-wool dyes**, IV. 208a  
— "benzidine" dyes, IV. 210d  
— dyes from stilbene, IV. 221a  
— mordant azo-wool dyes, IV. 213a
- Discharge** styles in textile printing, IV. 184d
- Discrasite**, I. 446b; IV. 16d
- Disinfectant** action of metals, IV. 24d  
—, bromidine, IV. 22b  
—, Burnett's fluid-, IV. 24a  
—, "Camphorlar," IV. 30a  
—, "Cadadyn," IV. 24d  
—, chloralum, IV. 24b  
—, chloride of lime (*see also* Bleaching powder), IV. 20c  
—, "Chlorox," IV. 20d  
—, "De-Chlor," IV. 21b  
—, "Electrozone," IV. 21b  
—, "Oxychloride," IV. 20d  
—, pinol, IV. 31a
- Disinfectants** (*see also* Antiseptics; Food preservatives), IV. 16d  
—, acids, IV. 23b  
—, alcohols, IV. 26b  
—, aluminium chloride, IV. 24b  
—, arsenic compounds, IV. 24c  
—, black, IV. 33d  
—, boric acid, IV. 20a  
—, bromine, IV. 20b, 22b  
—, carbolic acid, II. 308c; IV. 20b, 32a  
—, carbon dioxide, IV. 23a  
—, disulphide, IV. 20a  
—, Chick-Martin test, IV. 32c  
—, chlorinated phenol, IV. 34a  
—, chlorine, IV. 20b  
—, peroxide, IV. 22b  
—, chromic acid, IV. 24c  
—, coal-tar, IV. 29b  
—, cyanogen, IV. 23b  
—, fluorine, IV. 22d
- Disinfectants**, formalin (*see also* Formaldehyde), II. 297c, 306b; IV. 26c; V. 297c, 322b  
—, halogen, IV. 20a  
—, hydrocyanic acid, IV. 23b  
—, hydrogen peroxide, IV. 19a; VI. 346d  
—, hypochlorites, IV. 20b  
—, hypochlorous acid, IV. 21d  
—, iodine, IV. 22c  
—, lime, IV. 24a  
—, manganates, IV. 24b  
—, mercury compounds, IV. 25c  
—, nitric acid, IV. 19b  
—, nitro-aromatic compounds, IV. 30c  
—, nitrogen oxides, IV. 19b  
—, ozone, IV. 18c  
—, paraform, paraformaldehyde, IV. 26d  
—, permanganates, IV. 24b  
—, persulphates, IV. 20a  
—, phenol, *see* Disinfectants, carbolic acid.  
—, Rideal-Walker test, IV. 31d  
—, silver nitrate, IV. 26a  
—, sodium hydrogen sulphate, IV. 20a  
—, substituted diphenyl compounds, IV. 34a  
—, sulphur, IV. 19b  
—, sulphuric acid, IV. 19d  
—, testing, IV. 31c  
—, white, IV. 33d
- Disinfection**, mechanism, IV. 17a
- "Dispargen,"** IV. 34a
- Disperse** phase, III. 279b  
— rule, III. 292b
- Dispersing agents**, II. 391a, 427c; III. 280d
- Dispersion** of cellulose, II. 450b  
— "Dispersol," I. 40d
- Dissociation**, electrolytic, II. 536c  
— of molecules, II. 531c, 537c  
— "Dissociations" in acid-base reactions, VI. 248c
- "Dissolving Salt B,"** IV. 180c
- Distempers**, II. 415b; IV. 303a  
—, borax in, II. 50d  
—, casein in, II. 414b
- Distibonic acids**, I. 437b
- Distillation**, IV. 34b  
— and relative volatility, IV. 43c  
—, binary mixtures, IV. 41d, 50b  
—, Coffey still for spirit, I. 176d  
—, flash, IV. 34b  
—, fractional, IV. 39b, 48b  
—, laboratory, IV. 34b  
— of acetone-chloroform mixtures, IV. 40c  
— alcohol-water mixtures, IV. 39b  
— azeotropes, IV. 38c, 40a, d, 46c  
— under reduced pressure, IV. 41b  
— benzene-toluene mixtures, IV. 43b, 49d  
— water mixtures, IV. 37a  
— binary mixtures, IV. 41d

- Distillation** of completely miscible liquids, IV. 39d  
 — conjugate solutions, IV. 37c  
 — ether-water mixtures, IV. 36a, 46d  
 — liquid oxygen - nitrogen mixtures, IV. 42c  
 — partly miscible liquids, IV. 38c  
 —, partial, IV. 50a  
 — with partial condensation, IV. 49c, 51a  
**Distribution** number of anthocyanins, III. 341b  
**Distyrenes**, IV. 51c  
**"Disulphamin,"** IV. 52b  
**Dita bark**, I. 263a  
**Ditaine**, I. 203b  
**Ditamins**, I. 263a  
**Di- $\eta$ -tetradecyl ketone**, II. 183a  
**1:3-Ditetrazolyltriazene**, VI. 149d  
**1:4-Dithian**, IV. 380d  
**Dithian** methiodide, IV. 371c  
**Dithiol** for tin detn., II. 673a; IV. 52b  
**Dithionic acid**, detn., volumetric, II. 667b  
**Diufortan**, *see* Diuretin.  
**"Diuretin,"** IV. 52c  
**"Divers" beads**, helium in treatment, VI. 199c  
**Diversine**, IV. 52c  
**Divi-divi**, IV. 52d, 276d  
**Divinyl**, II. 154b  
 — acetylene, I. 87c  
**s-Divinylethylene glycol**, II. 156b  
**Dixanthogens**, V. 267b  
**Djavé fat**, I. 655a  
**D.N.T.** (dinitrotoluene), IV. 466c, 168b  
**Dobby**, V. 156b  
**Docimasy**, IV. 53a  
**Dodder oil**, II. 237a  
**Dodecylene**, II. 177d  
**Dolerite**, I. 656d  
**Doffer web**, V. 117c  
**Dog-tooth spar**, II. 203c  
**Dolerite**, III. 571a; IV. 53a  
**Dolomite**, II. 201a; IV. 53b  
 —, decomposition, II. 321c  
 — for glassmaking, V. 560c  
 — rock, IV. 51a  
 — spar, IV. 53c  
**Dolomitisation**, III. 361a; IV. 51b  
**Domesticine**, IV. 55a  
**isoDomesticine**, IV. 55a  
**Domestine**, IV. 55a  
**Domeykite**, IV. 55b  
**Donaxine**, VI. 125c, 403c  
**Donnan's** membrane - equilibrium, III. 288c  
**Dopa**, equilibria (*l*-3:4-dihydroxyphenylalanine), I. 317d; IV. 55c  
**Dop** brandy, II. 63c  
**Dorema ammoniacum**, I. 356c  
**Doremol**, IV. 55c  
**Doremone**, IV. 55c  
**"Dormigene,"** IV. 55c  
**"Dormiol,"** IV. 55d  
**Dorr** agitator and thickener, IV. 572a, c  
 — bowl classifier, VI. 103d  
**"Doryl,"** III. 94a  
**Doss**, IV. 55d  
**Dossetin**, IV. 55d  
**Double layer** of colloid particles, III. 284a  
**Doubling** and twisting, V. 151a  
**Doubly-refracting-spar**, II. 203c  
**"Doucil,"** VI. 144c  
**Douglas powder**, IV. 556b  
**Dowmetal**, I. 255d  
**Downs** electrolytic cell, III. 57d  
**Dracaenic acid**, IV. 50a  
**Draconic acid**, IV. 56a  
**Dracorubin**, IV. 56a  
**Dracyl**, IV. 55d  
**"Draft,"** II. 95c  
**Dragendorff's reagent**, I. 235c  
**Dragon's Blood**, IV. 55d  
**Drawing** of candles, II. 265c  
**Drechsel's extractor**, IV. 577c  
**Driers**, IV. 91b  
 —, cerium in, II. 511a  
 — for gases, IV. 79d  
**"Drikold,"** IV. 56a  
**Drop gum**, IV. 56a  
 — reactions (*see also under* elements and radicals), II. 579c  
 —, bibliography, II. 582c  
 — reagents, VI. 425d  
**Drosera rotundifolia**, IV. 56b  
**Droserone**, IV. 56c  
 — hydroxy-, IV. 56c  
**Druggist's bark** (cinchona), III. 128d  
**Drumme**, IV. 56d  
**Dry cleaning**, IV. 57a; IV. 68a  
 —, carbon tetrachloride in, II. 356a; IV. 57b  
 — solvents, tests, IV. 57d  
 — with trichloroethylene, I. 103b; IV. 57b  
**Dryer**, revolving plate, IV. 69c  
 —, — rabble, IV. 69c  
**Dryers**, agitator, IV. 73b  
 — band, IV. 77b  
 — compartment, IV. 62a  
 — double shell rotary, IV. 66c  
 — drum, IV. 74c  
 — for materials in lengths, IV. 70d  
**Dryer**, single cylinder paper, IV. 72b  
 —, — shell rotary, IV. 66a  
**Dryers**, rotary, IV. 65c  
 — spray, IV. 75d  
 — tumbler, IV. 68a  
 — tunnel, IV. 62a  
 — turbo, IV. 72d  
 — vacuum, IV. 62c  
 — vertical, IV. 68b  
**Dryer**, vacuum band, IV. 78a  
 —, — pan, IV. 73c  
**Dry gases**, reactivity, IV. 80b  
**"Dry ice"** (*see also "Drikold"*), II. 324d, 326d  
**Drying** (*see also* Dehydration), IV. 58a  
 — apparatus in analysis, II. 542b  
 — by drainage and settlement, IV. 58c  
 — evaporation, IV. 60d  
 — pressure, IV. 59a  
 — intensive, IV. 79c  
 — of fatty oils, reactions in, IV. 92b  
 — oils, *see* Oils, drying.  
 — on tentering machines, IV. 72a  
**Dry liquids**, boiling points, IV. 81a  
**Dryophant**, V. 426a; VI. 87b  
**Dry substances**, melting points, IV. 81b  
 —, retarded combustion, IV. 86b  
 —, vapour densities, IV. 80d  
**Duchn**, II. 488a  
**"Dudu-Dudu,"** II. 523b  
**Dufaycolor** film, II. 453a  
**Duff** producer, V. 380d  
**"Dulcin,"** IV. 93a  
**Dulcitol**, II. 285b, 290d; IV. 93a  
**Dulse**, I. 199b  
**Dumasin**, IV. 93b  
**Dumortierite**, I. 370c  
**Dumoulin's** liquid glue, V. 506a  
**Dung** salt or dunging salt, I. 478d; IV. 93b  
**Duodecyl alcohol**, IV. 93b  
 — aldehyde, IV. 93c  
**"Duotal,"** IV. 93c; VI. 141a  
**Du Pont** powder, IV. 518a  
**Duprene**, definition, IV. 93c  
 —, history, I. 74b, 87c; IV. 87b  
 —, prepn., I. 89b; II. 153d  
**Durain**, V. 351a  
**Duralumin**, I. 251d, 277a  
**Durangite**, I. 261d  
**"Durangus,"** IV. 93d  
**"Duranol"** dyes, I. 41b, 205c  
**Durene**, III. 539b  
**isoDurene**, I. 66d; III. 539b  
**Durenol**, IV. 93d  
**"Durez,"** IV. 93d  
**"Durite,"** IV. 93d  
**"Durocaine,"** I. 309d; IV. 93d  
**"Duron,"** IV. 93d  
**Duroprene**, *see* Duprene.  
**Durrha**, II. 482c  
**Durum** wheat, II. 76c  
**Dust**, adsorptive properties, IV. 95d  
 — clouds, stability, IV. 97a  
 — electrical ignition, IV. 99d  
 — properties, IV. 99a  
 — explosions, I. 180a; IV. 94a, 97a, 101b  
 —, precautions against, IV. 103b, 118d  
 — respirators, IV. 106d  
 — separation by filtration, IV. 99b  
 — various methods, IV. 98c  
**Dusts**, ignition temperatures, IV. 100a  
 —, industrial, I. 160a; IV. 94a  
 —, particle sizes in, I. 160a; IV. 94d, 98a  
 —, physiological effects, IV. 105d  
**"Duxite,"** IV. 120b  
**Duyk**, IV. 21d  
**Dyeing**, IV. 120c  
 — cellulose acetate and viscose rayon mixtures, IV. 145a  
 — rayon, IV. 138d  
 — cotton, after-treatment, IV. 131b  
 — and viscose rayon, IV. 145b  
 — with basic dyes, IV. 132a  
 — direct dyes, IV. 181a  
 — substantive dyes, IV. 131a

- Dyeing** cuprammonium rayons, IV. 138b  
 — fur, IV. 146a  
 — machines, IV. 130a  
 — rayon (see also Acetate silk dyes), IV. 137b  
 —, scouring and creping in, IV. 137c  
**Dyeings**, after-treatment by diazotising and coupling, IV. 131d  
 —, detection of metals (mordants) in, IV. 173a  
**Dyeing** silk, degumming, IV. 143d  
 — with azoic dyes, IV. 143c  
**Dyeings**, mixed, separation by adsorption, IV. 174a  
 —, —, — chromatographic analysis, IV. 174c  
**Dyeing**, spray, IV. 140b  
**Dyeings**, spectroscopic analysis, IV. 175b  
 —, stripping, IV. 145c  
**Dyeing**, theory, IV. 140b  
 — union goods, IV. 144d  
 — viscose rayons, IV. 138b  
 — with Aniline Black, IV. 137a  
 — azoic dyes, IV. 132d  
 — Indigosol, IV. 136b  
 — mordant dyes, IV. 136d  
 — Soledon dyes, IV. 136b  
 — vat dyes, IV. 135a  
 — wool and viscose rayon mixtures, IV. 145a  
 —, carbonising before, IV. 139c  
 —, chlorinating before, IV. 139b  
 —, fermentation vats in, IV. 143b  
 —, Goodall's process, IV. 140c  
 —, hydrosulphite vat in, IV. 143a  
 —, scouring in, IV. 139b  
 — with acid dyes, IV. 139d  
 — mordant dyes, IV. 141b  
 — azoic dyes, IV. 143c  
 — chrome dyes, IV. 141b  
 — Indigosol dyes, IV. 143b  
 — mordant dyes, IV. 141a  
 — Soledon dyes, IV. 143b  
 — vat dyes, IV. 142c  
**Dye printing**, IV. 175c  
**Dyer's Broom**, IV. 189a  
 — bugloss, I. 236d  
**Dyes**, acid-mordant, identification, IV. 155b  
 —, alizarin, see under Alizarin.  
 — amido, I. 305a  
 —, anthraquinone, see Anthraquinone dyes.  
 —, anti-halation, in photographic films, II. 451c  
 —, azo-, see Azo-dyes.  
 —, azoic, on cellulosic fibres, identification, IV. 157b  
 —, —, wool and silk, identification, IV. 156b  
 —, basic, IV. 127a  
 —, — mordant, identification, IV. 157d  
 —, —, on cellulosic fibres, identification, IV. 156c  
 —, bottoming, IV. 156a  
 —, detection, in caramel, II. 277b  
**Dyes**, direct cotton, components and performance, IV. 215c, 224c  
 —, —, dyeing with (see also Azo-dyes), IV. 127a  
 —, "Dispersol," I. 41a  
 — in casein plastics, II. 416d  
 — plastics, II. 416d, 470b  
 —, "Lithol," IV. 236a  
 —, luminescent oxidation, III. 23c  
 — "Monolite," IV. 236a  
 — "Monosol," IV. 236a  
 — mordant, co-ordination compounds, III. 335b  
 —, —, in dyeing operations, IV. 127d  
 — on cellulose acetate rayon, identification, IV. 172c  
 — fibres, identification, IV. 147b  
 — wool and silk, identification, IV. 155a  
 —, —, identification, IV. 194d  
 —, pigment, IV. 236a  
 — produced by oxidation, IV. 127c  
 —, substantive, on cellulosic fibres, identification, IV. 156c  
 —, —, wool and silk, identification, IV. 155c  
 —, sulphonated, I. 429a; VI. 449d  
 —, sulphur, on cellulosic fibres, identification, IV. 157a  
 —, synthetic, in world trade, I. 204d, 403c; VI. 147a  
 —, topping, IV. 156a  
**Dyestuffs**, see Dyes; Dyeing.  
**Dyes**, vat, on cellulosic fibres, identification, IV. 157c  
 —, —, wool and silk, identification, IV. 155d  
 —, —, solubilised, I. 428d  
 "Dumal," IV. 239a  
**Dynamite** (see also Nitroglycerin), IV. 239a  
 — cartridges, manufacture, IV. 230c  
 —, effect of heat, IV. 210a  
 — explosions, heat and temperature, IV. 240c  
 — explosive power, IV. 240b  
 — frozen, IV. 240d  
 — gelatine, IV. 241c, 243a  
 — kieselguhr, IV. 239b  
 — low- or non-freezing, IV. 242b  
 —, properties, IV. 239d  
**Dynamites**, ammonia, IV. 241b  
 —, ammonia-gelatine, IV. 242b  
**Dynamite**, sensitivity, IV. 240a  
**Dynamites**, non - kieselguhr, IV. 240d  
**Dynamite**, stability, IV. 240c  
 —, "straight," IV. 241a  
 —, sympathetic detonation, IV. 240c  
 — testing, IV. 243d  
 —, velocity of detonation, IV. 240b  
**Dynobel**, IV. 554c  
**Dysanolyte**, IV. 245a  
**Dyscrasite**, IV. 245a  
**Dysodile**, IV. 245b  
**Dysprosium**, II. 511c; IV. acetate, IV. 246c  
**Dysprosium** acetylacetone, IV. 246c  
 — bromate, IV. 246c  
 — bromide, IV. 246a  
 — carbonate, IV. 246c  
 — chloride, IV. 246a  
 — chromate, IV. 246b  
 — cyanoplatinite, IV. 246c  
 — ethyl sulphate, IV. 246b  
 — formate, IV. 246c  
 — hydroxide, IV. 246a  
 — iodide, IV. 246a  
 — nitrate, IV. 246b  
 — oxalate, IV. 246c  
 — oxide, IV. 245d  
 — oxychloride, IV. 246a  
 — phosphate, IV. 246b  
 — selenate, IV. 246b  
 — sulphate, IV. 246a  
 — sulphide, IV. 246a

## E

- Earlandite**, IV. 246b  
**Earth** almond, III. 119d  
**Earthenware**, common, VI. 8d  
**Earth**, infusorial, kieselguhr, III. 579a; IV. 239b  
**Earth-nuts**, I. 454c  
**Earths**, active, IV. 246d  
 —, in oil refining, contact distillation process, IV. 249d  
 —, —, processes, IV. 249c  
 —, —, percolation process, IV. 249c  
 —, —, pulp contact process, IV. 249d  
 —, —, regeneration, IV. 250a  
 —, adsorbent, activation, IV. 248c  
 —, rare, II. 507d, 511b  
 —, as catalysts, II. 350b  
 —, —, defn., gravimetric, II. 594b  
 —, qualitative reactions, II. 551a, 556d, 560b, 562b, 568c, 585b  
 —, separations, II. 514d, 594b  
 —, silicates, II. 150d  
**Earth-wax**, II. 506d  
**Eau de Javel**, Eau de Javelle, III. 36d, 64c; IV. 20d, 250c  
 — Labarraque, III. 36d, 64d; IV. 20c  
 — Luce, IV. 250c  
 — Vie, II. 62d  
**Ebonite**, IV. 250c  
**Ebulliometer**, IV. 250c  
**Ebullioscope**, IV. 250c  
**Eccaine**, IV. 250d  
**Ecgonine**, d- and l-, III. 224d, 225a  
 —, benzoyl-, III. 224d  
**Echineneone**, II. 401d  
**Echinopsine**, IV. 251a  
**Echitamidine**, I. 263c  
**Echitamine**, I. 263a  
**Echujin**, II. 387c  
**Eckain**, IV. 250d  
**Ecolite**, III. 575d  
**E. C. Powder**, IV. 518a  
**Ecu** silk, II. 18d  
**Edestin**, IV. 251b  
**Edingtonite**, IV. 253c  
 "Edinol," IV. 253c

- Edulcoration**, IV. 253c  
**Edwardsite**, II. 512b  
**Efflorescence**, IV. 253d  
 — of masonry, II. 128b  
**Egg fruit**, IV. 257a  
 —, hen's, IV. 253d  
 "Egols," IV. 257c  
 "Ehof," V. 260c  
**Ehrlich** 418 and 914, I. 491b, 492a  
**Eicosoic acid**, I. 454b  
 "Eikonogen," IV. 257d  
**Eiloart's extractor**, IV. 589a  
**Einstein's equation** for viscosity of sols, III. 290c  
**Eka-boron**, II. 511d  
**Eka-silicon**, V. 520c  
**Ekkain**, IV. 250d  
**Eksantalal**, IV. 257d  
 "Ektogan," IV. 258a  
**Elæis guineensis**, III. 238c, 243a  
**Elæomargaric acid**, IV. 258a  
**Elæoptene**, IV. 258a  
**Elæostearic acid**,  $\alpha$ - and  $\beta$ -, IV. 258a  
 **$\beta$ -Elæostearin**, oxidation, IV. 92b  
**Elaidic acid**, IV. 258d; VI. 184c  
 —, derivs., IV. 259b  
**Elaidin reaction**, IV. 258d  
 "Elarson," IV. 259c  
**Elastins**, VI. 21b  
**Elaterin**, IV. 259c  
**Elaterium**, IV. 259c  
**Elderberry**, IV. 259d  
**Elecampane**, I. 475b  
 "Electrargol," IV. 260c  
**Electrical endosmosis**, III. 283d  
**Electrodeposition** (*see also* under Analysis), IV. 260c  
**Electrodeposits**, testing, IV. 270d  
**Electrodes**, carbon, manufacture, I. 268d; II. 313c  
**Electrodispersion**, III. 281a  
**Electrogalvanising iron**, IV. 267d  
**Electro-kinetic potential**, III. 283d  
**Electrolysis**, Faraday's laws, IV. 261a  
**Electrolytic extraction** of metals, IV. 260d  
**Electron compounds** in alloys, VI. 282b  
 —, concentrations in alloys, VI. 283b  
**Electronic theory** in inorganic chemistry, IV. 272c  
 —, — organic chemistry, IV. 274d  
**Electron**, positive, I. 542d  
**Electrons**, I. 541a  
**Electro-osmosis**, III. 283d  
**Electroplating**, IV. 260c  
 —, boron in, II. 51a  
 —, with cadmium, II. 193a  
**Electrovalency**, III. 334a; IV. 272c  
 "Elektron," I. 255d  
**Elemene**, and tetrahydroelemene, IV. 276a  
**Elemi**, IV. 275a  
**Elemicin**, IV. 275d  
**Elemi** in lacquers, II. 469d  
**Elemol**, and tetrahydroelemol, IV. 276a  
**Eleusinin**, II. 188d  
**Eliasite**, VI. 151d  
**Eliquation**, IV. 276d  
**Elixir vitæ**, II. 520c  
**Ellagic acid**, II. 195a, 439a; IV. 15a, 276d  
**Elm-seed oil**, IV. 278c  
 "Elloxyl" protection of metals, III. 392c  
**Elutriation**, IV. 278d  
**Emanium**, I. 137b  
 "Embarin," IV. 278d  
**Embden ester**, V. 22a, 36b  
**Embden's scheme** of lactic acid formation in muscle, VI. 76b  
**Embelia ribes**, IV. 279a  
**Embelic acid** or embelin, IV. 279a  
**Embolite**, II. 107d, 181c, 516d; IV. 279a  
**Embossing**, V. 189a  
**Emerald**, I. 685b; IV. 279a  
 "Emerald, Brazilian," V. 513d  
**Emerald**, chromium in, III. 96b  
 —, copper, III. 355d; IV. 7d  
**Emeraldine**, VI. 419c  
 "Emerald, lithia," V. 513d  
 "Emerald, Oriental," III. 398d; V. 513d  
 "Emerald, Uranian," V. 513d  
**Emery**, I. 1a, III. 398d; IV. 279d  
 paper, I. 4b  
**Emetamine**, IV. 280d  
**Emetine**, IV. 280d  
 —, bismuthous iodide, IV. 282a  
 —, occurrence, II. 480d  
**Emicyparin**, VI. 87d  
**Emmenin**, VI. 269b  
**Emmens' acid**, IV. 483d  
**Emmensite**, IV. 483d  
**Emodin**, III. 116c  
**Emodinanthranol**, II. 120c  
**Emodin**,  $\omega$ -hydroxy-, V. 55c  
 —, in buckthorn, II. 120c  
 —, in cascara sagrada, II. 110d  
**Empire powder**, IV. 518a  
 "Empurin," I. 517d; IV. 282c  
**Empressite**, IV. 282c  
 "Emulgator 157," IV. 280c  
**Emulsification**, IV. 284a  
**Emulsifying agents**, II. 427c; IV. 281c  
 —, complex nitrogen derivs., *an.*, IV. 286c  
 —, from polyhydric alcohols, IV. 286c  
 —, mixed, IV. 286d  
 —, —, patents summarised, IV. 287-290  
 —, solid, IV. 286d  
 —, Turkey-red oils in, II. 421d  
**Emulsin**, II. 209d, 442c; IV. 282d  
 —, action on cellobiose, II. 442d  
**Emulsions**, IV. 284a; VI. 509d  
 —, aged, IV. 292b  
 —, biological, IV. 301a  
 —, casein in, II. 414b  
 —, chromatic, IV. 293c  
 —, concentration of disperse phase in, IV. 290b  
 —, cosmetic, IV. 303c  
 —, creaming, IV. 291a  
 —, determination of type, IV. 291c  
**Emulsions** for leather, IV. 302d  
 —, homogenisers for, IV. 295c  
 —, oil in water, IV. 284a  
 —, optical properties, IV. 293b  
 —, pharmaceutical, IV. 303c  
 —, phase inversion, IV. 293d  
 —, photographic, II. 450b  
 —, prepn., III. 292d; IV. 291c  
 —, size-frequency analysis, IV. 291b  
 —, stability, IV. 292b  
 —, Stoke's law for, IV. 291a  
 —, viscosity, IV. 292c  
 —, water in oil, IV. 291a  
**En**, III. 329c  
**Enamel**, boron in, II. 51a  
**Enamelling furnaces**, IV. 300d  
 —, iron suitable for, IV. 301c  
**Enamels** (*see also* Glass), IV. 303d, 307a; VI. 12d  
 —, fitting and mulling, IV. 300a  
 —, under-glaze colours, VI. 13a  
**Enantiotropic**, definition, line I. 1. 212c  
**Enargite**, III. 311c; IV. 307d  
**Endive**, IV. 308a  
**Endocamphene**, II. 238a  
**Endomminotriazoles**, VI. 150a  
**Enflourage**, II. 186b  
**English powder**, I. 201b  
**Engobe**, VI. 11a  
**Enhydros**, II. 517b  
**Enolase**, V. 27c; VI. 77a  
**Ensilage**, IV. 308b  
 losses, IV. 310c  
**Enstatite**, IV. 311a  
**Enterokinase**, IV. 311a  
**Enzyme** action, conditions influencing, IV. 312c  
 —, activators and inhibitors, IV. 312d  
 —, reaction kinetics, IV. 313c  
**Enzymes** (*see also* Fermentation, alcoholic; F., bacterial; F., mould), I. 303c; II. 99d; IV. 311a; VI. 395a  
 —, amylolytic, in cotton bleaching, II. 5b  
 —, dehydrogenases, IV. 315b  
 —, glycolytic, VI. 390c  
 —, in bryony root, II. 119c  
 —, degumming of silk, II. 18b  
 —, industry, IV. 315b  
 —, of yeast, II. 99d  
 —, oxidising, IV. 315b  
 —, proteoclastic, in dough, II. 76b  
 —, purification, IV. 313a  
 —, syntheses effected by, V. 48d, 57d; VI. 396b  
**Eosin**, IV. 316a, b  
 —, Methylene Blue stain for starches, II. 502d  
**Ephedine**, IV. 317b  
**Ephedra spp.**, IV. 316c  
**Ephedrine**, IV. 316c  
 **$\psi$ -Ephedrine** and related bases, IV. 316c  
 "Ephetonal," IV. 317c  
 "Ephetonin," IV. 317c  
**Epiborneol** and epi-isoborneol, IV. 318a  
**Epicamphor**, IV. 318c  
 —, hydroxy-, II. 31c, 245d  
 —, isonitroso-, II. 247a  
 "Epicarin," IV. 319a

- Epicatechin**, II. 435b  
*l*-**Epicatechin**, I. 11b  
**Epichitosamine**, II. 295c  
**Epichitose**, II. 205c  
**Epichlorohydrins**,  $\alpha$ - and  $\beta$ -, IV. 319a, 320b  
**Epicholestanol**, III. 89b  
**Epichinchonidine**, III. 153d  
**Epichinchonine**, III. 158a  
**Epicooprostanol**, III. 89b  
**Epidiolymite**, IV. 394b  
**Epidiorite**, IV. 320c  
**Epidosite**, IV. 320d  
**Epidote**, IV. 320c  
 — schist, IV. 320d  
**Epifucose**, II. 287c  
**Epiguanine**, VI. 200d  
**Epiphyrin alcohol**, VI. 71c  
**Epiphydrocinchonidine**, III. 162c  
**Epiphydrocinchonine**, III. 163d  
**Epiphydroquinidine**, III. 165b  
**Epiphydroquinine**, III. 166b  
**Epimerism of sugars**, II. 289b  
**Epinephrine** (U.S.P.), I. 145c  
**Epinephrine**, I. 145c, 147d  
 "Epinine," I. 147d; IV. 321a  
**Epiosine**, IV. 321a  
**Epiphase of carotenoids**, II. 308d  
**Epiphasic esters**, I. 137b, footnote  
**Epiquinidine**, III. 128a, 171d  
**Epiquinine**, III. 128a, 177b  
 "Epirenan," I. 147d  
**Epirhamnose**, II. 287c; IV. 321a  
 "Eponit," I. 153a  
**Epsomite**, IV. 321b  
**Epsom salts**, IV. 321b  
**Equulenin**, VI. 209a, c  
 —, synthesis, VI. 271a  
**Equilibrium**, chemical, II. 533c; IV. 338c  
 — constant, II. 533c; IV. 338c  
 — ester of fermentation, V. 22a  
**Equilin**, VI. 209a, c  
**Erbia**, IV. 322c  
**Erbium**, IV. 321b  
 — acetate, IV. 323d  
 — boride, IV. 323d  
 — bromate, IV. 323a  
 — bromide, IV. 322d  
 — carbonate, IV. 323c  
 — chlorate, IV. 322d  
 — hydroxide, IV. 322c  
 — iodate and iodide, IV. 323a  
 — nitrate and nitride, IV. 323c  
 — oxide, IV. 322c  
 — oxychloride, IV. 322d  
 — perchlorate, IV. 322d  
 — periodate, IV. 323a  
 — phosphates, IV. 323c  
 — platinocyanide, IV. 323d  
 — selenates, selenides and selenites, IV. 323b  
 — sulphate, IV. 323a  
 — sulphide, IV. 323a  
 — trichloride, IV. 322d  
 — trifluoride, IV. 322d  
**Erdin**, V. 58b  
**Erecthida oil**, IV. 323d  
**Eremite**, II. 512b  
**Eremophilone**, IV. 324a  
 —, hydroxy-, IV. 324a  
**Erepsin**, IV. 325c  
 — in cabbage, II. 182d  
**Ergine**, IV. 328a  
**Ergobasine**, IV. 330d  
**Ergochrysin**, IV. 332d  
**Ergoclavine**, IV. 327d  
**Ergocristine**, IV. 327c, 328d, 330b  
**Ergocristinine**, IV. 327c, 328d, 330b  
**Ergoflavin**, IV. 332d  
**Ergoline**, IV. 329b  
**Ergometrine**, IV. 327c, 328c, d, 330c  
**Ergometrinine**, IV. 327c, 328c, 330c  
**Ergonovine**, IV. 330d  
**Ergosine**, IV. 327c, 328c, d, 330c  
**Ergosinine**, IV. 327c, 328c, d, 330c  
**Ergostanes**,  $\alpha$ - and *allo*-, IV. 326a  
**Ergosterol**, IV. 325c  
 — from moulds, V. 57a  
 — in ergot, IV. 331c  
 — rice, II. 494b  
 —, irradiation, II. 201c  
**Ergostetrine**, IV. 330d  
**Ergotamine**, IV. 327d, 328d, 330b  
**Ergotaminine**, IV. 327c, 328d, 330b  
**Ergot**, assay, IV. 330d  
 —, detection, in flour and bread, IV. 332d  
**Ergothioneine**, IV. 332b  
**Ergotinine**, IV. 327b, 328a, 330a  
**Ergotocine**, IV. 330d  
**Ergot of rye**, *ergota*, IV. 326d  
**Ergotoxine**, IV. 327c, 328b, c, 329b, d  
**Ergot**, sugar in, II. 300c  
*Eriocaceae* spp., I. 457c; II. 231d; VI. 93b, 190a  
 "Ericin," IV. 333b  
**Eriocilin**, IV. 333b  
*Eriogon canadensis*, IV. 333c  
**Eriogon oil**, IV. 333c  
 "Erinoid," IV. 333d  
*Eriococcus coriaceus*, IV. 333d  
**Eriodictyol**, IV. 333d  
*Eriodictyon glutinosum*, IV. 333d  
**Eriodonol**, IV. 333d  
**Eriodyctionon**, IV. 333d  
**Erioglaucine**, IV. 334d  
**Eriubescite**, II. 32d; III. 341c  
**Eriubic acid**, II. 06d; IV. 334c  
 — derivs. and salts, IV. 335b  
 — in camelline oil, II. 237b  
 —, oxidation, II. 67b  
 — anhydride, IV. 335b  
**Eruicin**, IV. 335b  
 "Eruasin," IV. 335c  
**Erythrene**, II. 154b  
**Erythric acid**, I. 243d  
**Erythrin**, IV. 335c  
**Erythrite**, I. 169a; III. 214b; IV. 335c  
**Erythritol**, I. 501c; II. 296b  
 — formins, V. 327b  
 — from moulds, II. 296b; V. 51c  
 —, reaction with hydrogen iodide, II. 173d  
**Erythroapocyanine**, III. 529a  
**Erythrocytes of blood**, II. 19d  
**Erythroglaucin**, V. 54d  
**Erythrophleins**, II. 381b  
**Erythrophloic acid**, IV. 336a  
*Erythrophloeum* spp., alkaloids, IV. 335d  
**Erythroquin** reaction, III. 136c  
**Erythro-resinotannol**, I. 618b  
**Erythrosin**, IV. 316c, 336b  
**Erythroxyanthraquinone**, I. 206a, 212d, 216a  
 — 2:4-disulphonic acid, I. 390b  
 — 2-monosulphonic acid, I. 390b  
*Erythroxyllum coer.*, *E. spp.*, III. 222d  
**Erythrozyme**, IV. 337b  
 "Esbit," I. 153a  
**Eseramine**, II. 200a  
**Eseré nut**, II. 198d  
**Eserethole**, II. 199d  
**Eseridine**, II. 200b  
**Eserine**, II. 198d  
**Eseroline**, II. 199b  
**Esop** test, IV. 550b  
**Esparto**, I. 199a  
 — cellulose, xylan in, II. 303c  
 — paper, II. 462d  
 "Essence of pearl," V. 605d  
**Essigsprit**, I. 44a  
**Esterases**, IV. 314a, 347d; VI. 395b, 396d  
 "Ester gum," I. 3a  
 — in lacquers, II. 400a, 472b  
**Esterification**, IV. 337b, 347a  
 — by enzymes, IV. 347d  
 —, catalytic (*see also* Catalysis), II. 428b; IV. 337c, 338d; VI. 222c, 257d  
 —, constitutional relationships, IV. 340c  
 —, effect of structure of alcohols, IV. 343d  
 —, practical applications, IV. 343c, 372a  
 —, with aliphatic acids, constitutional effects, IV. 340d  
 —, — aromatic acids, constitutional effects, IV. 342a  
 —, — dibasic acids, constitutional effects, IV. 341c  
 —, — ketonic acids, constitutional effects, IV. 341d  
 —, direct, IV. 344b  
 —, velocity constant, IV. 345b  
 —, effect of neutral solvents, IV. 340a  
 —, — water, IV. 339d  
 — of dibasic acids, IV. 346b  
 — sulphonic acids, IV. 347d  
 —, steric hindrance, IV. 340d  
 — theories, IV. 348a  
 — vapour phase, IV. 340b, 347c  
 —, velocity constant, IV. 337c, 339c, 343b, 349b  
**Esters of polyhydric alcohols as emulsifying agents**, IV. 286c  
 —, prepn., II. 372a; IV. 347a  
 —, reaction with alcohols, VI. 397c  
 —, reduction, II. 374c  
 —, sulphonic, as plasticisers, II. 448c  
 "Eston," IV. 349d  
 "Estoral," IV. 349d  
**Estrichgips**, II. 130b, 131a; IV. 349d  
**Eta acid**, *c*-acid, IV. 349d  
**Étain de glace**, I. 694  
**Etard's reaction**, I. 194b  
**Etching solutions**, V. 600d



- "Etelon"** I.G., IV. 350a  
**Ethane**, IV. 363b  
 —, 2-bromo-1-iodo-, IV. 373d  
 —, chloropentabromo-, II. 320d  
 —, detn., (*see* Methane, detn.), II. 684a  
 —, *s*-dibromo-, IV. 373c'  
 —, dibromotetrafluoro-, II. 323b  
 —, *s*-dichloro-, I. 19c; IV. 374a  
 —,  $\alpha$ -dichloro- $\alpha\beta\beta$ -tetra-bromo-, II. 321a  
**1:2-Ethanediol**, IV. 377b  
**1:1-Ethanediol** diethyl ether, I. 34c  
**1:2-Ethanedithiol**, IV. 381b  
**Ethane**, hexabromo-, II. 320c  
 —, hexachloro-, I. 97d, 105a; II. 173c, 223c, 351a  
 —, hexafluoro-, II. 323b; IV. 361c  
 —, pentabromo-, IV. 358a  
 —, pentachloro-, I. 97d, 100d, 104d; IV. 359c  
**Ethanes**, *as*- and *s*-tetrachloro-, I. 98a; IV. 359c  
 —, trichloro-, I. 98a; IV. 359c  
**Ethanesulphonic acid**, IV. 370d  
**Ethane**, tetrabromo-, IV. 357c  
 —, *s*-tetrachloro-, I. 97d, 98a  
 —, tetrachlorodibromo-, II. 321a  
**Ethanethiol**, IV. 369c  
**Ethane**, tribromo-, IV. 357c  
 —,  $\alpha\alpha\beta$ -tribromo- $\alpha\beta\beta$ -trichloro-, II. 321a  
 —,  $\alpha\alpha\beta$ -trichloro-, I. 98a  
**Ethanol**, *see* Alcohol; **Ethyl alcohol**.  
**Ethenyl trichloride**, IV. 359c  
**Ether** (*see also* Anesthetic ether; **Ethers**), IV. 364a  
**Etherates**, IV. 385a  
**Ether**, autooxidation, IV. 387b  
 —, detn., II. 683a  
 —, explosions, prevention, IV. 388a  
 —, luminescent oxidation, III. 23b  
 —, manufacture, IV. 385c  
 —, peroxides, IV. 351, 388a  
**Ethers**, IV. 350a  
 —, action of heat and light, IV. 352a  
 —, addition compounds, IV. 351d  
 —, polyhydric, as emulsifying agents, IV. 280c  
**"Ethobrome"**, I. 559d  
**Ethocaine** (*see also* "Æthocaine"), II. 34b  
**Ethoxide**,  $\beta$ -hydroxy-, sodium, IV. 377d  
**Ethyl**, IV. 353c  
**Ethylacetate**, I. 34c  
**Ethyl acetate**, I. 28a, 51a; IV. 383d  
 —,  $\beta$ -bromo-, IV. 373c  
 —, catalytic production, II. 535d  
 —, formation, II. 423b  
 —, from *Penicillium digitatum*, V. 51b  
 —,  $\beta$ -hydroxy-, IV. 373a  
 —, production, I. 56d  
 —, specification, II. 472b  
 —, acetoacetate, I. 62a  
 —,  $\alpha$ -bromo-, I. 63c  
**Ethyl acetoacetate**,  $\alpha$ -dibromo-, I. 63c  
 —, semicarbazone, I. 63d  
 —, alcohol (*see also* Alcohol), II. 126d  
 —,  $\beta$ -amino-, III. 94a  
 —,  $\beta$ -bromo-, IV. 373b  
 —,  $\beta$ -chloro-, IV. 375b  
 —, detn., in vapours, II. 683a  
 —, from moulds, V. 51a  
 —,  $\beta$ -nitro-, IV. 379d  
 —, specifications, II. 472b  
 —,  $\beta\beta\beta$ -tribromo-, I. 559d  
 —, vapour pressure, I. 180a  
 —, viscosity, I. 180b  
**Ethylallene**, I. 240c  
**Ethylamine**, IV. 353c  
 —, from acetylene, I. 84d  
 —, tri- $\beta$ -hydroxy-, I. 307a  
**Ethyl ammonium selenite**, IV. 367d  
**Ethylisoamylmalonylurea**, I. 365d  
**Ethylaniline**, IV. 383c  
 —,  $\alpha$ -hydroxy-, VI. 402a  
**Ethyl anthranilate**, IV. 383d  
**antimonate**, IV. 356c  
 arsenate, IV. 356c  
 arsenite, IV. 356c  
 — benzate, I. 680d; IV. 383d  
 borate, IV. 356c  
 boride, IV. 356d  
 borosulphate, II. 53c  
 bromide, IV. 356d  
 $\alpha$ -**Ethyl** -  $\alpha$ -**bromobutyryl** - carbamide, I. 441a  
**Ethyl butyrate**, II. 181c; IV. 383d  
 —, isobutyrate, II. 181c  
**Ethylbutyric acid**,  $\alpha$ - and  $\beta$ -, II. 271c, d  
 $\alpha$ -**Ethylbutyrolactone** acetic acid, VI. 262c  
**Ethylcarbazole** in chemical warfare, III. 10c  
 —, production, III. 11d  
**Ethyl carbamide**, IV. 359d  
 — carbonate, II. 322a; IV. 358a  
 — carbylamine, IV. 360c  
 — cerotate, II. 516c  
**Ethylchloramine**, IV. 354d  
**Ethyl chloride**, IV. 358b  
 — chlorocarbonate, II. 322a  
 — cyanate, III. 181c; IV. 384a  
 — compounds, *see also under* Diethyl and Ethane.  
**Ethylcupreine**, III. 101b  
**Ethyl isocyanate**, IV. 359d  
 cyanide, IV. 360a  
 isocyanate, IV. 360c  
 — cyanine T, III. 515b  
 cyanurate, IV. 360d  
 — isocyanurate, IV. 361a  
 — diazoacetate, III. 590a  
 —, reaction with camphene, II. 238a  
**Ethylidibromoamine**, IV. 354d  
**Ethylidibromoarsine** production, III. 11d  
**Ethylidichloramine**, IV. 354d  
**Ethylidichloroarsine** production, III. 11d  
**Ethyl-di-iodoamine**, IV. 354d  
**Ethyl-di-iodostibine**, I. 433d  
**Ethyl dimethylcarbinol**, II. 359d  
**Ethyl diselenide**, IV. 367c  
 — disulphide, IV. 370c  
**Ethyl ditelluride**, IV. 372a  
**Ethylene**, IV. 372b  
**1:2-Ethylene** acetals, I. 37a  
**Ethylene bromohydrin**, IV. 373b  
 — bromoiodide, IV. 373d  
 — bromotrichloro-, II. 320d  
 — chlorohydrin, IV. 375b  
 — chlorobromide, IV. 375c  
 — chloroiodide, IV. 375d  
 — chlorotribromo-, II. 320d  
 — isocyanate, IV. 375d  
 — cyanide, IV. 376a  
 — cyanohydrin, IV. 375d  
 —, detn., II. 683a  
 — diacetate, IV. 373b  
**Ethylenediamine**, IV. 376a  
 — reagent for dyes, IV. 149c, 157d  
**Ethylene dibromide**, IV. 373c  
 —, bromo-, IV. 357c  
 —, prepn., II. 110b  
 dichloride, IV. 374a  
 —, as insecticide, II. 350d  
 —, *as*-dichloro-, IV. 374c  
 —, *s*-dichloro-, I. 101a; IV. 7b, 374c  
 —, *cis*- and *trans*-dichloro-, I. 87d, 97b  
 —,  $\alpha$ -dichloro- $\beta\beta$ -dibromo-, II. 320d  
**Ethylenediethylamine**, IV. 370c  
**Ethylene-*as*-diethyldiamine**, IV. 370c  
 — diethyl sulphide, IV. 381c  
 — di-iodide, IV. 379c  
 — dimethyl sulphide, IV. 381c  
**Ethylenedinitramine**, IV. 480c  
**Ethylene dinitrate**, IV. 379d  
 dithiocarbonate, IV. 381c  
 dithiocyano-, IV. 381d  
 —, exchange reaction with deuterium, VI. 374d  
 from acetylene, I. 79c  
 glycol (*see also* Glycol), I. 19c; IV. 377b  
 dinitrate, IV. 480d  
 — monoacetate, IV. 373a  
 —, mono- and di-formin, V. 326a  
 —, *n*-butyl ether, II. 179b  
 —, monoethers, II. 443a  
 —, — in lacquers, II. 470a  
 —, hydrogenation, VI. 374c  
**Ethylenimine**, IV. 370c  
**Ethylene mercaptan**, IV. 381b  
 — monoacetate, IV. 373b  
 —, monochloro-, IV. 374c  
 —, nitro-, IV. 379c  
 —, oxide, IV. 379d  
 —, as fumigant, II. 361c; V. 395b  
 —, bromo-, IV. 380b  
 —, chloro-, IV. 380b  
 —, detn., II. 683b  
 —, oxido-,  $\alpha\beta$ -dicarboxylic acid, from *Monilia*, V. 51d  
 —, ozonide, IV. 380b  
 —, perchloro- (*see also* Ethylene, tetrachloro-), I. 97b, 99b, 104b  
 —, production, II. 428b  
 —, selenocyanate, IV. 380d  
 —, sulphide, IV. 381c  
 —, tetrabromo-, II. 320c  
 —, tetrachloro- (*see also* Ethylene, perchloro-), I. 104b; IV. 375b

- Ethylene**, tetrafluoro-, II. 323*b*  
 —, tetraiodo-, II. 281*b*  
 —, thiocarbamide hydrochloride, IV. 381*d*  
 —, trichloro-, *see* Ethylene, trichloro-  
 —, trichloro-, antineuralgic, III. 86*a*  
 —, —, as solvent, I. 102*b*; II. 356*b*  
 —, —, prepn., I. 99*c*; II. 428*d*  
 —, —, properties, I. 97*d*; 100*b*; IV. 374*d*  
 —, trithiocarbonate, IV. 381*c*  
**Ethyl** ester number, III. 235*a*  
 — esters as perfumes, IV. 383*d*  
 — ether (*see also* Ether), IV. 384*a*  
 —, —, detn., in vapours, II. 683*a*  
 —, —,  $\alpha\beta$ -dichloro-, I. 21*c*  
 —, —,  $\beta\beta$ -dichloro-, IV. 389*a*  
 —, —, ethyl  $\alpha\beta$ -dichloro-, I. 21*c*  
 —, —, production, II. 428*b*  
 — ethylene, II. 177*a*  
 — ethylsulphonate, IV. 371*a*  
 — ferrocyanide, IV. 361*b*  
 — fluoride, IV. 361*b*  
**Ethylformal**, I. 34*b*  
**Ethyl formate**, IV. 361*c*  
 —, —,  $\beta$ -chloro-, IV. 375*c*  
 —, —,  $\alpha\alpha$ -dichloro-, IV. 362*a*  
**Ethylglyoxaline**, 4- $\beta$ -amino-, IV. 331*d*  
**Ethylhydrazine**, IV. 362*a*  
 — sulphonate, potassium, IV. 362*b*  
**Ethylhydrocuprein**, III. 137*a*, 161*b*, 167*c*  
**Ethyl** hydrogen peroxide, IV. 360*b*  
**Ethylhydroxylamine**,  $\alpha$ - and  $\beta$ -, IV. 362*d*  
**Ethyl** hypochlorite, IV. 363*d*  
 — hyponitrite, IV. 361*b*  
**Ethylidene** acetamide, IV. 381*d*  
 — alkyl ethers, IV. 382*d*  
 — biuret, IV. 382*a*  
 — bromiodide, IV. 382*b*  
 — chlorobromide, IV. 382*c*  
 — chlorosulphide, IV. 382*c*  
 — chlorosulphonic acid, IV. 383*c*  
 — diacetate, I. 37*d*, 91*d*; IV. 381*d*  
 — dibromide, IV. 382*b*  
 — dibutyrate, I. 37*d*  
 — dichloride, IV. 382*c*  
 — diethyl ether, I. 34*c*  
 — di-iodide, IV. 383*a*  
 — dipropionate, I. 37*d*  
 — dipropyl ether, IV. 382*d*  
 — disulphonic acid, IV. 383*c*  
 — ethoxyacetate, IV. 383*b*  
 — ethylene oxide, IV. 383*b*  
 — ethyl propyl ether, IV. 382*d*  
 — glycol, I. 21*a*  
 — hydroxysulphonic acid, IV. 383*b*  
**Ethylideneimine**, IV. 383*a*  
**Ethylidene** methyl propyl ether, IV. 382*d*  
 — sulphonic acids, IV. 383*b*  
**N-Ethylindole**, I. 84*c*  
**Ethyl** iodide, IV. 364*b*  
 — iodoacetate in warfare, III. 8*c*  
 —, prepn., III. 11*d*  
 — lactate in lacquers, II. 470*b*  
**Ethyl** laurate, IV. 384*a*  
 — mercaptan, IV. 369*c*  
 — metaphosphate, IV. 366*d*  
 — methylidiphenylurea, II. 480*c*  
**Ethylmorphine** hydrochloride, IV. 7*c*  
**Ethyl** nitrate, IV. 364*d*  
 — nitrate,  $\beta$ -iodo-, IV. 356*b*  
 — nitrite, IV. 365*b*  
**Ethylnitroamine**, IV. 354*d*  
**Ethyl** nitrogen chloride, IV. 354*d*  
 —, —, nonylate, IV. 384*a*  
 —, —, orthocarbonate, IV. 358*a*  
 —, —, orthophosphate, mono-, IV. 366*c*  
**Ethylpelargonic** acid, VI. 204*b*  
**Ethyl** pentasulphide, IV. 370*d*  
**p-Ethylphenol** in castor, II. 410*d*  
**Ethyl** phenylacetate, IV. 384*a*  
 —, —, phosphates, IV. 366*c*  
 —, —, phosphite, mono-, IV. 367*a*  
 —, —, phosphites, IV. 366*d*  
**Ethylphosphoric** acid, mono-, IV. 366*c*  
**Ethylphosphorous** acid, IV. 367*a*  
**Ethylpiperazine**,  $\beta$ -amino-, IV. 377*a*  
**Ethylpropylacetic** acid, VI. 205*c*  
**Ethylisopropylacetic** acid, VI. 205*c*  
**N-Ethylquinaldine** from acetylene, I. 84*c*  
**Ethylquinclidone** oxime, III. 164*c*  
**Ethyl** sacchylate, IV. 384*a*  
 — selenides, IV. 367*c*  
**Ethylseleninic** acid, IV. 367*b*  
**Ethyl** selenium compounds, IV. 367*b*  
 — selenomercaptan, IV. 367*b*  
 — sulphate, di- $\beta$ -bromo-, IV. 369*a*  
 — sulphates, mono- and di-, IV. 368*a*  
 — sulphide, IV. 370*a*  
**Ethylsulphinic** acid, IV. 370*c*  
**Ethyl** sulphite,  $\beta$ -chloro-, IV. 369*c*  
 —, —, mono-, IV. 369*b*  
**Ethylsulphonic** acid, IV. 370*d*  
**Ethyl** sulphoxide, IV. 370*b*  
**Ethylsulphuric** acid, IV. 368*a*  
 —, —,  $\alpha$ - and  $\beta$ -bromo-, IV. 368*d*  
 —, —, chloride, IV. 368*c*  
**Ethyl** sulphhydrate, IV. 369*c*  
 — telluride, IV. 372*a*  
 — tetrasulphide, IV. 370*d*  
 — thiocarbimide, IV. 371*d*  
 — isothiocyanate, IV. 371*d*  
 — titanate, IV. 372*a*  
 — trisulphide, IV. 370*d*  
 — "Etoscol," III. 558*d*  
**Etu**, III. 338*b*  
 — "Eubornyl," IV. 389*b*  
 — "a-Eucaine," IV. 389*b*  
 — "b-Eucaine," I. 369*a*, 667*a*; IV. 389*b*  
 — borate, II. 34*b*  
**Eucairite**, IV. 389*d*  
**Eucalyptol**, *see* 1:8 Cineole, and under Cineole.  
**Eucalyptus globulus**, antimalarial properties, IV. 31*a*  
 —, —, globulol from, II. 25*b*; VI. 13*b*  
**Eucalyptus macrorhyncha**, IV. 391*a*  
 — *spp.*, dyes from, IV. 33*d*  
 —, —, essential oils, II. 25*b*; IV. 389*d*  
**Eucarvone**, IV. 391*b*  
 — from *d*-carvone, II. 408*a*  
 — "Eucatropine," IV. 401*a*  
**Eucazulene**, I. 119*d*  
**Euchrysin** 3R, I. 132*a*  
**Euclease**, I. 685*b*; IV. 392*a*; VI. 13*c*  
 — "Eucodal," IV. 392*b*  
 — "Eucoleine," IV. 392*b*  
 — "Eucoil," II. 431*d*; IV. 392*b*  
**Eucryptite**, IV. 392*b*  
 — "Eucupin," III. 168*b*; IV. 392*c*  
**Eudalene**, IV. 270*a*, 325*a*, 392*c*, 393*a*  
**Eudesmin**, IV. 392*c*  
**Eudesmol**, IV. 393*a*  
**Eudialyte**, IV. 394*a*  
**Eudidymite**, IV. 394*b*  
 — "Eudrenine," IV. 394*b*  
 — "Eugallol," IV. 394*b*  
**Eugenia aromatica** (cloves from, III. 204*c*)  
 — *caryophyllata*, eugenol from, III. 207*b*; IV. 394*c*  
**Eugenol**, IV. 394*c*  
 — *iso*Eugenol, *cis*- and *trans*-, IV. 397*d*, 398*c*  
**Eugenol**, bromo-derivs., IV. 396*d*  
 — *iso*Eugenol, bromo-derivs., IV. 400*a*  
**Eugenol** from clove oil, IV. 395*a*  
 — *iso*Eugenol from eugenol, IV. 397*d*  
**Eugenolglucoside**, IV. 397*c*  
**Eugenol** in essential oils (*see also* *Eugenia spp.*), II. 240*c*, 269*c*, 411*a*; III. 183*c*  
 —  $\alpha$ -naphthylurethane, IV. 397*c*  
 —, —, 5-nitro-, IV. 396*c*  
 — *iso*Eugenol, 5-nitro-, IV. 400*a*  
**Eugenol** perfumes, IV. 400*b*  
 — phenylurethane, IV. 397*c*  
 — *iso*Eugenol, IV. 397*d*  
 —, —, acyl derivs., IV. 399*c*  
 —, —, *cis*- and *trans*-isomers, IV. 398*c*  
 — phenylurethanes, *cis*- and *trans*-, IV. 399*a*  
 — *s*-trinitrobenzene compound, IV. 399*d*  
 —, —, vanillin from, IV. 399*a*  
**Eugenyl** acetate, I. 436; IV. 396*d*  
 — *iso*Eugenyl acetate, *cis*- and *trans*-, IV. 399*d*  
**Eugenyl** alcohol, IV. 397*c*  
 — *iso*Eugenyl benzoate, *cis*- and *trans*-, IV. 399*d*  
**Eugenyl** carbonate, IV. 397*b*  
 — *iso*Eugenyl carbonate, IV. 400*a*  
**Eugenyl** chlorocarbonate, IV. 397*b*  
 — methyl ether, IV. 394*d*, 397*a*  
 — *iso*Eugenyl methyl ether, IV. 397*d*, 400*a*  
**Eugenylphosphoric** acid, IV. 397*c*  
**Eugenyl** sulphate, potassium, IV. 397*b*  
**Euglenarhodone**, II. 400*d*, 401*a*

- "*Eukodal*," IV. 392b, 400b  
 "*Eulatin*," IV. 400b  
**Euler** and **Diels**' synthesis, I. 401c  
**Euonymin**, II. 387d; IV. 400c  
**Euonymite**, *see* Dulcitol.  
**Euonymol**, IV. 400c  
**Euonymus**, *E. atropurpureus*, IV. 400c  
**Euonysterol**, IV. 400c  
**Eupad**, IV. 27f, 400c  
**Eupatheoscope**, VI. 288b  
*Euphorbia resinifera*, *E. spp.*, IV. 400c; IV. 56d, 277b  
**Euphorbic acid**, euphorbol and euphorbone, IV. 100d  
**Euphorbium**, IV. 400c  
**Euphotide**, V. 409b  
*"Euphthalmis"*, IV. 401a  
*"Euphyllin"*, I. 326a; IV. 401a  
**Eupittonic acid**, eupittonic acid, IV. 401a  
*"Euprine vernade"*, IV. 401d  
*"Euporphin"*, II. 118c; IV. 401d  
*"Euguinine"*, IV. 401d  
*"Euresol"*, IV. 401d  
**Eurhodines**, I. 563d, 568a  
**Eurhodols**, I. 563d, 568a, 569c  
*"Eurobin"*, IV. 402a  
**Europic carbonate**, IV. 104b  
   chloride, IV. 403d  
   hydroxide, IV. 404a  
   iodate, IV. 404a  
   nitrate, IV. 404b  
   nitrite, IV. 404c  
   oxide, IV. 403d  
   phosphate, IV. 404b  
   platinocyanide, IV. 104b  
   sulphate, IV. 404b  
**Europium**, II. 511c; IV. 402a  
   —, organic salts, IV. 104c  
   —, triple nitrate, IV. 104c  
**Europous carbonate**, IV. 104d  
   —, chloride, iodide and sulphate, IV. 104c  
*"Euscopol"*, IV. 405a  
**Eusol**, IV. 21d, 400c  
*"Eustenit"*, IV. 405a  
**Euterpene**, IV. 392a  
**Euxanthic acid**, IV. 405a; VI. 87d  
**Euxanthone**, VI. 424c  
**Euxenite**, II. 19c; IV. 321c, 405a; VI. 169a  
**Evaporation**, IV. 405a  
   — from a supersurface layer, III. 605a  
   — in analysis, II. 543a  
   — high vacuum, IV. 414a  
   — multiple effect, IV. 406d  
   — steam boilers, IV. 405d  
   — of acid liquors, IV. 413c  
   — delicate liquors, IV. 414a  
   —, rate, III. 451c  
   —, solar, of brine, IV. 411c  
   —, special cases, IV. 414d  
   —, spray, IV. 414c  
   — under reduced pressure, IV. 406a  
**Evaporator**, salting type, IV. 412a  
**Evaporators**, film, IV. 409b  
   —, steam heated, IV. 406a  
**Evaporator with forced circulation**, IV. 412c  
**Everitt's salt**, III. 471c  
**Evernic acid**, IV. 415b  
*"Eupan, eipan sodium"*, I. 368c, 623a; IV. 415b  
*Evodia meliaefolia*, I. 620b; IV. 415b  
**Evodiamine**, *isoevodiamine*, IV. 415c, d  
*Evodia rutacearpa*, alkaloids, IV. 415b  
**Evodine**, IV. 415c  
**Evonymin**, II. 387d; IV. 400c  
*"Exalgin"*, IV. 416d  
*"Exaltolide"*, IV. 416d  
*"Exalton"*, IV. 416d  
*"Exaltone"*, III. 601b  
**Excoecarin**, excoecaronc, VI. 136b  
**Exhaustive methylation**, I. 311d  
*"Exolon"*, I. 4a; IV. 417a  
**Expansion coefficients**, measurement, IV. 4c  
**Explosif P**, IV. 461d  
**Explosions**, gaseous (*see also* Detonation), IV. 417a  
   —, at high initial pressures, IV. 447b  
   —, auto-ignition m., IV. 436a  
   —, defn. of dissociation constants, IV. 444d  
   —, — heat capacities, IV. 444d  
   —, effect of pressure on limits, IV. 428a  
   —, excitation lag m., IV. 415b  
   —, heat losses m., IV. 411c  
   —, ignition pressures and knock-ratings, IV. 419d  
   —, nitrogen-activation m., IV. 416a  
   —, peroxides m., IV. 419, 452a  
   —, pressures developed m., IV. 410b  
   —, pressure-time data, IV. 412b  
   —, radiations from, IV. 411a  
   —, shock waves m., IV. 435a, 439a  
   —, stages in, IV. 435b, 440d  
   —, time-lags and pressures, IV. 451b  
*"Explosion wave"*, IV. 434b, 438a  
**Explosive D**, IV. 483c  
   — O<sub>2</sub>, IV. 515c  
   — power tests, IV. 547d  
**Explosives**, II. 525a; IV. 453d  
   —, brisant, IV. 555d, 561a  
   —, coal mine, IV. 552d  
   —, —, effect of sheathing, IV. 561a  
   —, —, flame from, IV. 552c, 558a  
   —, —, safe use, IV. 558a  
   —, —, substitutes for, IV. 502c  
   —, —, testing galleries, IV. 557a  
   —, flame from, IV. 521d, 558a  
   —, in firedamp, effect of solid particles, IV. 559a  
   —, —, ignition by pressure wave from, IV. 559d  
   —, initiatory, IV. 535a  
   —, as detonants, IV. 550b  
   —, liquid air, IV. 545d  
   —, oxygen, IV. 545d  
   —, moisture tests, IV. 540c  
   —, mortar test, IV. 548b  
**Explosives**, nitrobenzene, IV. 465a  
   —, nitrocellulose (*see also* Nitrocellulose), II. 461b; IV. 501c  
   —, nitrohydrocarbon, IV. 405a  
   —, permitted, *see* Permitted explosives.  
   —, secondary flame from, IV. 559a  
   —, sensitiveness to heat, IV. 552a  
   —, Sprengel, IV. 545b  
   —, stability tests, IV. 487c, 547a  
   —, testing, IV. 546c  
**Extensometer**, Chompi, II. 78b  
**Extraction apparatus**, industrial, IV. 562d  
   —, laboratory types, IV. 575b  
   batteries, IV. 564c  
   —, counter-current, in laboratory models, IV. 590c  
   —, grease, VI. 135a  
   —, in diffusion batteries, IV. 566b  
   —, micro-apparatus, IV. 583d  
   —, percolators, IV. 575b, 577b  
   —, large-scale apparatus, IV. 583b  
   of fine material, IV. 571c  
   liquids, IV. 574c  
   —, injection method, IV. 581d, 588c  
   —, perfluvination method, IV. 581d, 585c  
   —, with immiscible solvents, IV. 581a  
   —, solids, classifier for, IV. 509d  
   tanks, IV. 562a  
   with continuous infusion, IV. 579c  
   —, distillation of the solvent, IV. 572d  
   —, intermittent infusion, IV. 580d  
   —, non-aqueous solvents, IV. 570a  
   —, without corks or joints, IV. 578a  
**Eykman's formula**, V. 546b  
**Fabiatrin**, I. 160c; III. 413a  
**Fabrics**, *see also* Finishing textile fabrics.  
   —, belt stretching process, V. 187d  
   —, breaking, conditioning or dampening, V. 187c  
   —, calendaring, V. 188a  
   —, drying stiffened, V. 187a  
   —, finishing pastes for, V. 189a  
   —, fireproofing, V. 210c  
   —, woollen, milling, raising, shearing, V. 200a  
   —, —, pressing, raising, steam-igning, tentering, V. 206c  
   —, —, scouring, V. 204d  
   —, —, setting and shrinking processes, V. 205c  
**Factice**, *Factic*, IV. 590a  
**Factor Z** in fermentation, V. 11b

- Factory bark** (cinchona), III. 128*d*
- Fahlers**, IV. 590*a*
- Fahlors**, IV. 590*a*
- Faktis**, IV. 590*a*
- Famatinite**, III. 341*c*; IV. 308*a*
- Fanal colours**, IV. 591*a*
- "Faraday's gold"**, III. 270*d*, 289*c*; VI. 109*b*
- Faraday's laws of electrolysis**, IV. 261*a*; VI. 237*d*
- Farinograph**, Brabender, II. 78*b*
- Farnesal**, IV. 591*a*
- Farnesene**, IV. 591*c*
- Farnesenic acid**, IV. 591*a*
- Farnesol**, II. 261*b*; IV. 591*a*
- "Fast Bases (I.G.)"**, IV. 231*b*
- Fat**, Balam, II. 32*b*
- , detn., in chocolate, III. 80*d*
- , in feeding stuffs, IV. 592*d*, 601*d*
- , liquoring, III. 551*b*; IV. 302*d*
- , production by moulds, V. 57*b*
- Fats and oils**, edible, IV. 251*b*
- , Dika, IV. 3*d*
- , effect on concrete, II. 118*b*
- , emulsion in digestion, IV. 301*a*
- Fat**, Sengkawang-, II. 31*c*
- Fats**, hardened or hydrogenated (*see also* Hydrogenation), II. 426*d*; VI. 177*b*
- Fat**, Shorea, II. 31*c*, *d*
- Fats**, hydrolysis, VI. 41*a*
- , saponification, VI. 40*d*, 388*d*
- Fat**, soentai, II. 32*b*, foot-note —, "Teglam," II. 32*c*
- , Tongkawang-, II. 31*c*
- Fauser process**, I. 337*a*
- Favas**, I. 585*c*; III. 575*c*
- Faversham Powder**, IV. 553*c*
- Fayalite**, IV. 591*d*
- Fayence**, IV. 591*d*
- F.D.A.** test of disinfectants, IV. 32*d*
- Feather-alum**, I. 289*a*; IV. 591*d*
- Feathering** of candles, II. 260*d*
- Feather-ore**, IV. 591*d*
- Feculose**, IV. 592*a*
- Feeding meat and bone meal**, IV. 597*c*
- , meal, IV. 597*c*
- , stuffs, IV. 592*a*
- , —, analysis, IV. 592*a*, 601*d*
- , —, ash constituents, I. 503*c*; IV. 593*c*, 597*d*, 603*c*
- , —, energy equivalents, IV. 600*a*
- , —, manurial value, IV. 598*a*
- , —, mineral accessories, IV. 597*d*
- , —, mineral constituents in, I. 503*c*; II. 183*c*; IV. 593*c*, 597*d*, 603*c*
- Fehling's solution**, I. 648*d*
- Feigl's test**, I. 471*c*
- Feldmann still**, I. 345*b*
- Feldspar**, *see* Felspar
- Feld's process**, I. 340*d*
- Felite**, II. 141*b*
- Fellic acid**, I. 690*a*
- Felsite**, III. 32*d*
- Felspar**, I. 264*d*, 291*c*; II. 187*c*; VI. 1*a*; VI. 126*a*
- Felting of wool**, V. 206*a*
- "Femargin"**, IV. 330*b*
- Fenchane**, V. 4*a*
- cycloFenchene**, II. 254*c*; V. 5*d*
- Fenchenes**, V. 4*b*
- Fenchol**, V. 6*a*
- isoFenchol**, V. 6*b*
- Fenchone**, V. 6*d*
- , separation from camphor, II. 258*b*
- isoFenchone**, V. 7*c*
- Fenchyl alcohol**, V. 6*a*
- isoFenchyl alcohol**, II. 256*b*; V. 6*a*
- Fenchyl chloride from pinene**, II. 250*c*
- Fenchylene**, *see* Fenchenes.
- isoFenchyl esters**, II. 255*d*
- Fennel**, V. 8*a*
- , essential oil, V. 8*b*
- "Feran"**, I. 278*d*
- Ferberite**, V. 8*c*
- Ferganite**, II. 393*b*
- Fergusonite**, II. 512*c*; V. 8*c*; VI. 169*a*
- Fermentactyl**, V. 8*d*
- Fermentable substances**, V. 9*b*
- Fermentation**, acetic, I. 14*a*; V. 46*a*
- , acetone production, II. 109*c*, 471*d*; V. 15*a*
- , alcoholic (*see also* Alcohol; Brewing; Fermentation, bacterial; Fermentation, mould; Glycolysis; Yeast), V. 8*d*
- , —, bacterial, V. 45*c*
- , —, co-enzymes, V. 15*b*
- , —, Mg and Mn ions in, V. 18*c*
- , —, auto-, of yeast, glycogen formation, V. 15*a*
- , bacterial (*see also under* Fermentation, alcoholic), I. 176*c*; II. 429*b*; V. 41*a*
- , —, effects of conditions, V. 45*c*
- , —, hydrogen production, II. 169*c*; V. 44*a*; VI. 332*d*
- , —, of glycerol, V. 44*d*
- , butyl alcohol, II. 169*c*, 471*d*
- , butyric, II. 179*c*; V. 45*a*
- , by dry yeast and yeast juice (*see also* Yeast, dried), V. 15*a*
- , —, yeast, equations, V. 27*b*
- , carbon dioxide from, II. 324*c*
- , *coli-typhosus* group, V. 42*b*
- , enzymic equilibrium of hexose diphosphate, V. 26*b*
- , glycerol production, V. 23*d*; VI. 41*b*
- , heat, V. 11*b*
- , hexosephosphates, V. 20*b*
- , hydrolysis of phosphoric esters, V. 22*c*
- , lactic, bacterial, V. 41*c*
- , —, of cabbage, II. 183*c*
- , *Monilia*, V. 51*d*
- , mould (*see also* Fermentation, alcoholic; Fermentation, bacterial), V. 48*b*
- , —, citric acid production, III. 188*a*; V. 49*b*
- , —, oxalic acid production, V. 49*a*
- , of hexosediphosphoric ester, V. 21*b*
- Fermentation of hexosemono-phosphate**, V. 30*d*
- , panary, II. 75*b*
- , phosphoric esters in (*see also* Fermentation, alcoholic; Glycolysis), II. 295*d*
- , phosphorylated inter-mediate compounds, V. 24*b*
- , propionic, bacterial, V. 41*d*
- , pyruvic acid theory, V. 23*b*
- , rate of, by yeast, V. 10*c*, 14*c*
- , reactions of yeast in, V. 39*d*
- , succinic acid, bacterial, V. 43*a*
- , yeast, redistribution of phosphorus, V. 40*d*
- , yeasts in, II. 97*a*
- Ferment**, yellow respiratory, IV. 311*d*
- Fernambuco wood**, II. 68*a*
- Fernandinite**, V. 60*a*
- Feronia gum**, V. 60*a*
- Ferric and Ferrous compounds**, *see also* Iron.
- Ferric-alumina**, I. 290*a*
- , chloride, chlorination by, II. 428*d*
- , ferricyanide, III. 476*c*
- Ferricyanides**, detn., volumetric, II. 654*d*, 655*a*
- , from ferrocyanides, III. 465*a*
- , prepn. by chemical oxidation, III. 465*a*
- , —, electrolytic oxidation, III. 475*c*, *d*
- , qualitative reactions, II. 569*c*
- Ferrite**, V. 60*a*
- Ferritungstite**, V. 60*b*
- Ferro-alloys**, manufacture, II. 217*c*
- Ferroaxinite**, I. 560*d*
- Ferrobrucite**, II. 119*b*
- "Ferroclore"**, IV. 21*d*
- Ferrochrome**, III. 105*d*
- Ferrocyanides**, analysis, III. 511*b*
- , detn., II. 655*a*, 707*c*
- , prepn., III. 465*a*
- , —, from coal gas, III. 466*c*
- , —, cyanides, III. 466*c*
- , —, nitrogenous organic matter, III. 466*b*
- , —, spent oxide, III. 467*d*
- , —, thiocyanates, III. 469*c*
- , —, by dry process, III. 467*c*
- , —, wet process, III. 468*b*
- , qualitative reactions, II. 569*c*
- Ferrosilicon**, manufacture, II. 217*c*
- Ferrotungsten**, V. 60*b*
- Ferrous ammonium ferrocyanide**, III. 471*c*
- , hydroxide, action, on carbon tetrachloride, II. 355*d*
- , manganese tungstate, II. 198*d*
- , phosphate, II. 25*b*
- , potassium ferrocyanide, III. 471*c*
- Ferrucite**, V. 60*b*
- Ferriamite**, V. 60*c*
- Fertiliser analysis**, preparation of samples, V. 85*c*
- , ammonium nitrate, V. 65*c*
- , sulphate, V. 65*a*
- , borax, remedial, I. 505*a*; II. 35*a*; V. 74*a*

- Fertiliser**, carbon dioxide as, II. 326b  
 —, gypsum, V. 73d  
 —, hoof and horn, V. 66b  
 —, leather waste, V. 66c  
 —, lime, V. 74a  
 —, marl, V. 74a  
 —, nitrate of soda, V. 65b  
**Fertilisers**, mealmeal, V. 66c  
 —, mixed or compound, V. 73b  
 — or manures, V. 61a  
 —, potassium salts, V. 74a  
 —, relative value, V. 74b  
**Fertiliser**, saltpetre, V. 65b  
 —, superphosphate, V. 67d, 69d  
**Ferulic acid**, isoferulic acid, V. 60c, 61a  
**Fervanite**, V. 61a  
 — "*Fesemco*" slate, IV. 117c  
**Festbitumen**, V. 354b  
**Fetthol**, II. 26c  
**Fiberloid**, II. 443b, 480a  
**Fibre**, African, I. 161a; V. 108b  
 —, caroa, V. 108b  
 —, detn., IV. 593a, 602c  
 —, flax (see also *Flux*), V. 159b  
 —, —, scutching, V. 160d  
 —, hemp (see also *Abaca fibre*), V. 162c  
 —, indigestible, IV. 593a, 602c  
 —, kitul, V. 168b  
 —, Mexican, V. 168b  
 —, Palmyra, V. 168b  
 —, pineapple, I. 458d; V. 168b  
 —, pita, V. 168b  
**Fibres**, alginate, I. 202a; V. 124b  
 —, animal, silk, V. 86a  
 —, artificial, or rayon, V. 112a  
 —, electrical spinning, V. 128b  
 —, bast or soft, V. 158d, 159b  
 —, casein, V. 115c  
 —, cellulose, see *Cellulose*; Dyeing; *Fibres*, artificial, or rayon.  
 —, cotton, V. 135a  
 —, from seeds and fruits, V. 158d  
 —, gelatin, V. 115d  
 —, glass, V. 114c, 594b  
 —, leaf or hard, V. 158d  
 —, nylon, V. 126a  
 —, protein, V. 115b  
 —, superpolyamide, V. 125b  
 —, superpolymer, V. 125b  
 —, synthetic, V. 113b, 124d  
 —, vegetable, V. 158c  
 —, vinyl acetate and chloride, V. 126b  
 —, wool and related animal, V. 96a  
**Fibrin** in blood, II. 19d, 22c  
**Fibrinogen** in blood serum, II. 19d, 22c  
**Fibroin**, II. 17b; V. 86b, 90a  
**Fibrolite**, I. 370b; V. 169c  
 — "*Fibrolysin*," V. 169c  
**Fichtelite**, V. 169c  
**Fick's law** of diffusion, III. 606c, 607c  
**Ficocerylic acid** (see also *Fig wax*), V. 170c  
**Ficusin**, see *Fig*.  
*Ficus* spp., see *Fig*; *Fig wax*.  
**Fig**, V. 170c  
 — wax, V. 171a  
**Filament** electric lamps, V. 171c  
 — lamp design, V. 172a  
**Filaments**, carbon, V. 171d, 179b  
 —, —, flashing, V. 170d  
 — for thermionic valves, V. 179d  
 —, lamp, coiling, V. 170d  
 —, oxide-coated cathode, V. 180a  
 —, tungsten, V. 171b, 178a, 179a  
 —, —, "offsetting," V. 178c  
 —, —, thorated, V. 179d  
**Filbert**, V. 180b  
**Filicic acid**, V. 181c  
**Filicin**, V. 181c  
**Filicinic acid** butanone, V. 181c  
**Filicitanic acid**, V. 181a  
**Filitannic acid**, V. 181a  
**Filite**, Italian, IV. 519a  
*Filix mas*, V. 180d  
**Fillers** in magnesium oxy-chloride cement, II. 136c  
 — plastics, II. 476b  
**Filling fabrics**, V. 187a  
**Filmarone**, V. 182a  
**Filmcolor**, II. 453a  
**Film** manufacture, dopes for, II. 448a  
 —, photographic, II. 446a  
**Filosome**, II. 403c  
**Filter paper**, V. 182b  
 — "*Filtrol*," IV. 248c  
**Finings**, II. 102a; V. 505a; VI. 24b  
**Finishing** cotton cloth by etherifying agents, V. 193a  
 — with synthetic resins, V. 191c  
 — staple fibre cloths, V. 184a  
 crepe fabrics, V. 202d  
 effects, "permanent," V. 190d  
 — fabrics with cellulose ethers, V. 192c  
 — rayon cloths, plant and processes, V. 199c  
**Finishings**, cotton, classified, V. 190a  
**Finishing** textile fabrics (see also *Bleaching*), V. 183a; VI. 509c  
 — woollen and worsted fabrics, V. 205a  
 — yarns, V. 183b  
**Finnemanite**, V. 207c  
**Fire-clay**, V. 207c  
 — damp, II. 323d, 344c; IV. 441d, 552d, 559d  
 —, helium in, V. 349d  
 — extinction and prevention, V. 208b  
 — extinguishers, carbon tetrachloride in, II. 356a  
 —, chemical, V. 210b  
 —, foam, V. 208d  
 — hose cloth, V. 195d  
**Fireproofed** timber, tests, V. 217c  
**Fireproofers** and glowproofers, V. 213c  
**Fireproofing** of fabrics, V. 210c  
 — timber, V. 215c  
**Fireproof** paints, V. 226a  
**Fire-retarding** chemicals, V. 220c  
 — tube test, V. 219a  
**Fire**, silver, I. 1b  
**Fischer's salt**, III. 219b  
**Fischer - Tropsch synthesis**, II. 425b; V. 378b; VI. 333d, 378d  
**Fisetin**, V. 226d  
 — degradation, II. 60b  
**Fish** fermentation, V. 59c  
 — liver oils, composition, III. 247a, 250a  
 — manure, III. 246a  
 — meal, IV. 597b; V. 80d  
 — oil lubricants, V. 235c  
 — oils, IV. 85b; V. 226d, 230b  
 —, hydrogenated, edible, V. 234c  
 —, refining, V. 232d  
 —, vitamins A and D from, V. 234a  
**Fiske's extractor**, IV. 580c  
**Flagstone**, V. 235d  
**Flame**, V. 236b  
 — colorations, II. 547c, 680a  
 — penetration test, V. 219b  
**Flameproof** cotton and rayon fabrics, V. 198a  
**Flame** propagation in closed tubes, IV. 433a  
 — gaseous explosions, IV. 420d  
 —, velocity and compression waves, IV. 430a, 433a  
**Flames**, gas, calorific value, V. 240b  
 —, cool, IV. 422c, 424c, 429a  
 —, gaseous products from, IV. 417b; V. 244d  
 —, radiation from, V. 241d, 243c  
**Flame** temperatures, V. 240a  
 — types, V. 238a  
 —, uniform movement, IV. 430d  
 — velocity, influence of conditions on uniform, IV. 432a  
 —, — tube diameter on uniform, IV. 431d, 432a  
**Flammivore** V. 58a, IV. 550a  
**Flash lights**, v. 251a  
 — reducing agents, IV. 521d  
**Flavaniline**, I. 39a; V. 252b  
**Flavanone** or dihydroflavone, II. 519a; V. 252b  
**Flavanones**, relation to chalcones, II. 519a  
**Flavanthrene**, I. 394d, 399d  
**Flavanthrene**, I. 205c, 206a, 412d, 419d; V. 253b  
**Flavaspidic acid**, V. 181c  
**Flavellagic acid**, II. 105a; V. 181c  
**Flavenol**, V. 253d  
**Flaveosin**, I. 133c  
 — "*Flavianic acid*," III. 417d, foot-note; V. 253d  
**Flavin** enzyme, V. 33a  
 —, vegetable dyestuff, V. 253d  
**Flavinduline**, V. 254a  
 — O, I. 570b, 572b  
**Flavine** or acriflavine, I. 134b, 135d; IV. 30b  
**Flavogallol**, V. 254b  
**Flavogallone**, V. 254b  
**Flavogallonic acid**, V. 254b  
**Flavoglaucin**, V. 54c  
**Flavoline**, V. 255a  
**Flavone**, V. 255a, 257b  
 —, 1:3-dihydroxy-, III. 118d  
 —, 5:7-dihydroxy-4'-methoxy-, I. 11b, 12b  
 — in bran, II. 61a  
 — cacao red, II. 188b

- Flavone** occurrence, II. 440a  
**Flavones**, relation to chalcones, II. 518d  
*iso*Flavone, V. 258c  
**Flavonol**, V. 260a, 261a  
**Flavophosphine**, I. 133b  
**Flavopurpurin**, I. 206a, 212d, 224c  
 —, 3-nitro-, I. 228b  
**Flavorodin**, V. 262b  
**Flavourings**, butyric esters in, II. 181b  
**Flavoxanthin** (*see also* Carotenoids), II. 398d, 399d; V. 262c  
**Flax**, II. 416b; V. 159b  
 —, composition and dimensions, V. 161c  
 —, fibre,  $\alpha$ -cellulose content, V. 162b  
 —, pectins, V. 161d  
 —, roughing, hackling and preparing, V. 161a  
 —, shives and tow yarn, V. 160d  
 —, wax, V. 262c  
**Flèches d'amour**, VI. 101a  
**Fleitmann's test**, I. 470b  
**Flemingia congesta**, V. 262d  
**Flemingia**, V. 262d  
**Flint**, II. 517c; V. 262d  
 —, building, II. 138a  
**Flocculation** values, III. 285c  
**Flocons** in silk, II. 18a  
 "Floral hydrometers," III. 221b  
**Florencite**, V. 263c  
**Flores cinæ**, V. 263c  
**Floribundine**, floripavine, floripavidine, V. 263c  
 "Floriscinol," II. 422b  
**Florida earth**, IV. 217b  
**Floridean starch**, I. 200d  
**Floriditol**, I. 200d  
**Floridoses**, floridoside, I. 200c; VI. 88a  
 "Flosal," I. 303a  
**Floes-ferri**, I. 450d  
 "Flotagen," V. 207a  
**Flotation** process, V. 263d; VI. 500c  
 —, reagents, V. 260a, 269a  
**Flour**, composition, II. 74d  
**Flower of iron**, I. 450d  
**Fluavil**, fluavile, V. 269c; VI. 158d  
**Fluellite**, I. 264c, 280a  
**Fluid** heat transmission, IV. 415a  
**Fluoboric acid**, II. 40c  
**Fluocerite**, V. 269c  
**Fluocollophanite**, III. 294a  
**Fluorammine**, phenylhydrazine from, VI. 300c  
**Fluoranthene**, V. 269c  
**Fluoranthenequinone**, V. 270a  
**Fluorene**, V. 270c  
 —, formation, II. 195a, 139a  
**Fluorenone**, V. 272a  
**Fluorescein**, V. 272c  
**Fluorides**, detection and detn. in food, V. 298c  
 —, detn., colorimetric, II. 673b  
 —, —, gravimetric, II. 607c, 656d  
 —, —, volumetric, II. 650d  
 —, drop reaction, II. 582a  
 —, in butter, II. 167d  
 —, qualitative reactions, II. 576a  
**Fluorinating agents**, V. 278c  
**Fluorine**, V. 273a  
 —, compounds, antiseptic and physiological properties, IV. 22d; V. 282a  
 —, detn., spectroscopic, II. 602a  
 —, free, in fluorspar, II. 215b  
 —, halogen compounds, V. 277a  
 —, oxides and oxyacids, V. 277c  
 —, reactions, II. 350a; V. 275d, 278a  
**Fluorite**, V. 283a  
**Fluoroborate**, sodium, II. 50c  
**Fluorocyclene**, V. 282d  
**Fluoroform**, V. 283a  
**Fluorosulphonic acid**, V. 279b  
**Fluor-spar**, fluor or fluorite, II. 25b, 215a; V. 283a  
**Fluosilicates**, V. 282c  
**Flux**, V. 284b  
**Fly agaric**, I. 300d  
**Foaming**, prevention, V. 288d  
**Foams**, III. 279c; V. 285a  
 —, accelerated liquid/gas reactions in, V. 288d  
 —, interface conditions in, V. 285d  
 —, stability, V. 286a  
 —, technical uses, V. 288a  
**Fobbing**, II. 95d  
*Fœniculum vulgare*, *F. capillare*, V. 6d, 8b  
**Fœnugreek**, V. 289c  
 "Fogging" of metals, III. 370b  
**Foliarin**, II. 386b; VI. 88a, 92c  
**Food** bottling and canning, V. 290b  
 —, dyes in, detection, V. 300b  
 —, gas storage, V. 293b  
 —, metallic contamination in, V. 292b  
 —, preservation, V. 290b  
 —, preservatives, V. 296a  
 —, legal and medical aspects, V. 306c  
 —, regulations, V. 308b, 609, foot-note  
**Foods**, foreign substances in, V. 306c  
**Food** storage, control and effect of carbon dioxide, II. 326b; V. 293d  
 —, effect of humidity, V. 293c  
**Fool's parsley**, I. 160d; III. 324d  
 "Foraminate," VI. 181d  
*Foraminifera* spp., coral from, III. 360b  
 "Forgerin," V. 310b  
**Forging** alloys, I. 252b  
**Formaldehyde** (*see also* Disinfectants, formalin; Food preservatives), V. 310b  
 —, aqueous, V. 317a  
 —, as antiseptic, IV. 26c; V. 322b  
 —, preservative, V. 297c  
 —, compound, with bromal, II. 106b  
 —, casein plastics, II. 414a, 410c  
 —, detection and detn., V. 297d, 321d  
 —, from carbon monoxide, II. 350d; V. 316b  
 —, hydrocarbons, V. 310b  
 —, methanol, catalysts and process, V. 310b, 313a  
**Formaldehyde** monomer, gaseous and liquid, V. 317a  
 —, phenol resin (*see also* "Bakelite"), II. 422d; V. 321a  
 —, polymers, V. 318d  
 —, production, II. 427c  
 —, reactions, V. 320a  
**Formalin**, *see* Disinfectants; Formaldehyde.  
**Formals**, I. 34a  
**Formamide**, V. 322c  
**Formamidine**, V. 322d  
 "Formamine," I. 326a  
 "Formamol," VI. 200d  
 "Forman," V. 322d  
**Formanilide**, V. 323a  
 —, from carbon monoxide, II. 350d  
**Formates**, detn., V. 305d  
 —, from carbon monoxide, II. 350d  
 —, qualitative reactions, I. 53c; II. 569d; V. 305d, 324c  
**Formic acid**, *see also* Formates.  
 —, as antiseptic, IV. 27d  
 —, detection in acetic acid, I. 53c  
 —, esters and salts, V. 324d  
 —, from mould fermentation, V. 50c  
 —, in food, detection and detn., V. 305d  
 —, prepn. and properties, V. 323a  
 —, dehydrogenase, V. 44b  
 —, hydrogenlyase, V. 44b  
 "Formicin," V. 326a  
 "Formidin," V. 326a  
 "Formin," I. 326a  
**Formins**, V. 326a  
 "Formol" (*see also* Formaldehyde), IV. 26c  
**Formolites**, V. 327c  
**Formomonetin**, V. 259c  
**Formoprene**, I. 89b  
**Formosanine**, V. 327d  
 "Formosul," IV. 148c, 149c  
**Formosul** G, reagent for dyes, IV. 148c, 149c  
 "Fornitral," V. 327d  
**Forsterite**, V. 328a  
 "Forton," V. 328a  
 "Fouadin," I. 439a; II. 432d  
 "Fournau 189, 270 and 417," I. 489b, d  
**Fouling** of ships' hulls, protection against, III. 383b  
**Fowler's solution**, V. 328a  
**Foxberry**, V. 328a  
**Fragarianin**, fragarin, V. 328b  
**Fragarol**, II. 106b; V. 328c  
**Frankelite**, III. 538a; V. 328c  
**Francolite**, I. 449d  
**Frangula**, V. 328d  
 —, emodin, II. 410d; V. 328d  
**Franguloside**, I. 197d  
**Frangulin**, I. 197d, 198a; V. 328d; VI. 88a  
**Franguloside**, VI. 88a  
**Frankincense**, V. 328d  
**Franklinite**, V. 328d  
 "Frankonit," IV. 248c  
**Fraxetin**, V. 329a; VI. 279c  
**Fraxin**, III. 413a; VI. 88a, 279c  
**Fraxinellone**, III. 602c  
*Fraxinus excelsior*, V. 329a; VI. 88a  
**Fraxitannic acid**, V. 329a

- Freestone, V. 329a**  
**Freezing** mixtures, explosion risk, V. 329d  
 — or cooling mixtures, V. 329b  
**Freibergite**, IV. 590c  
**Fremontite**, I. 303d  
**French berries**, I. 560a  
**"French chalk,"** I. 162c  
**French polish, V. 329d**  
 — Poudre B, IV. 518c  
**"Fresol,"** III. 120a  
**"Freundlich** sorption isotherm," II. 540a; III. 282d  
**Freund's acid, V. 329d**  
**Friar's Balsam**, IV. 28d  
**Frick** process for carbon dioxide production, II. 327a  
**Friction**, sensitiveness of explosives to, IV. 551d  
**Friedel-Crafts** reaction, II. 363d; VI. 250b  
**Friedrich's** extractor, IV. 587b  
**Fritillaria**, alkaloids, V. 330a  
**Fritillaria spp.**, V. 330a  
**Fritillarine**, fritilline, V. 330b  
**Fritimine**, V. 330b  
**Frit kiln**, VI. 6b  
**Frits** and glazes, VI. 2c  
**Fritting**, VI. 5d  
**Froehde's** reagent, III. 321c  
**Frothers** (flotation process), V. 263d, 266c  
**Froth-flotation** process, V. 263d  
**Fructolysis**, VI. 71a  
**Fructose** (see also Levulose), II. 282b, 286a  
 — in milk, II. 303a  
**Fructosidase**, IV. 313b  
**Frühling's** extractor, IV. 581d  
**Fruits**, dried, spraving, VI. 209d  
 — storage, effect of ethylene, V. 295b  
**"Fuadin,"** see "Fouadin."  
**Fuchsia**, I. 576c  
**Fuchsine**, adsorption by rice protein, II. 502d  
**Fuchsisenecionine, V. 330c**  
**Fuchsine**, chromium m., III. 96b  
**Fucin**, I. 200a  
**Fucitol, V. 330c**  
 —, trityl, V. 330d  
**Fucoidin**, I. 200a  
**Fucosan**, I. 199c, 200a  
**Fucose**, II. 287c  
**Fucosol, V. 330d**  
**Fucosterol**, I. 199c, 200c  
**Fucoxanthin** (see also Carotenoids), I. 201a; II. 308a; V. 330d  
**Fucus vesiculosus** I. 199b, 201d; V. 330d  
**Fuel** (see also under Carbonisation: Coal carbonisation: Fuel, gaseous; Motor fuel), V. 331a  
 — "Fuel, colloidal," V. 361a  
**Fuel, gaseous** (see also Bottle gas; Fuel), II. 157b  
 —, liquid, from coal, V. 378b  
 — "Fullpulver 02," IV. 467a  
**Fuel oil**, III. 423d; V. 378a, 379a  
 — oils, production, II. 425d  
 —, pulverised, V. 361a  
**Fuels** from coal, V. 360c  
 —, gaseous, cal. val., V. 332c  
 —, liquid, cal. val., V. 332c
- Fukugenetin, isoFukugenetin, V. 381a**  
**Fukugetin, V. 380a**  
**Fukugi, V. 380a**  
**Fuller's** earth (see also Adsorption; Montmorillonite), IV. 217a; V. 381c  
 —, Japanese, VI. 182a  
**Fulminates**, IV. 535d; V. 381b  
**Fulminic acid, V. 382d**  
**Fulminuric acid**, Ehrenberg's, V. 387a  
**isoFulminuric acid, V. 386a**  
**Fulminuric acids,  $\alpha$ - and  $\beta$ -, V. 385a, 386c**  
**Fulvenes**, III. 534b, c  
**Fulvic acid, V. 53d**  
**Fumaric acid** from mould fermentation, V. 50b  
 — and maleic acids, V. 387a  
 —, identifying tests, V. 388a  
**Fumarine** (see also Protopyne), V. 388d  
**Fumes**, particle size, IV. 95b  
**Fumigant** toxicity, time-concentration curves, V. 391b  
**Fumigatin, V. 51a**  
**Fumigation**, chloroquern, V. 397b  
 against vermin and pests, V. 388d  
 —, bactericidal action, V. 391b  
 —, carbon dioxide, II. 361c; V. 391d  
 —, disulphide, II. 312c, 311a; V. 390b  
 —, tetrachloride, II. 311a; V. 390d  
 —, chlorobenzene m., II. 311a  
 —, coal tar naphtha, V. 397d  
 —, *o*- and *p*-dichlorobenzene, V. 397a  
 —, ethyl and methyl formates, V. 397d  
 —, ethylene dichloride, V. 396d  
 —, — oxide, II. 361c; V. 395b  
 —, hydrocyanic acid, III. 164b; V. 392d  
 —, hydrogen sulphide, V. 397d  
 —, methyl bromide, V. 397a  
 —, nitrobenzene, II. 311a  
 —, pentachlorethane, V. 396d  
 —, phosphine, V. 397d  
 —, potassium thiocarbonate in, II. 311a  
 —, pyridine, II. 311a  
 —, sulphur dioxide, V. 395a  
 —, tetrachloroethylene, I. 99c  
 —, toxicity detn. of reagents, V. 380b  
 —, trichloroethylene, I. 103d; V. 397a  
 —, — mixtures, V. 396d  
 —, warning gas m., V. 391b  
**Fungicides**, furfural, V. 401b  
 —, copper, II. 30d; III. 355d, 358b  
 —, xanthates as, II. 313d  
**Fungi** containing ergosterol, IV. 325c  
**Fungisterol** in ergot, IV. 331c  
**Funiculosin, V. 55c**  
**2-Furaldehyde, see Furfuraldehyde.**  
**Furan, V. 398a**  
 —, derivs., nomenclature, V. 400b  
 —, 2-hydroxymethyl-, -5-carboxylic acid, V. 52a  
 —, ethyl-, V. 400b
- Furanose** sugars, II. 282d  
**Furan**, reactions, V. 399c  
**Furfural** or furfuraldehyde, V. 400c  
**Furfuraldehyde** ethylacetal, I. 36c  
 — from bran, II. 62d  
**Furfural** from cellulose, II. 402c  
 —, oats, II. 489c  
 —, synthetic resins, V. 410b  
**Furfuran, V. 398c**  
**Furfurine, V. 402c**  
**Furfural** from pentoses (see also Furfural), II. 287b  
**Furfuryl alcohol**, V. 400b, 401d  
 —, in coffee, II. 198b  
**Furil, V. 402a**  
 —  $\alpha$ -dioxime, prepn. and use as Ni reagent, II. 612c; V. 102c  
**Furine, V. 402c**  
**Furnaces**, assay, I. 519d  
**Furoic acid, see Furfural.**  
**Furoin, V. 402a**  
**Furunculin, V. 402d**  
**Furyl alcohol, see Furfural.**  
**Furze**, VI. 125a  
**Fusain, V. 351a**  
**Fusanols, V. 402d**  
**Fusarium spp.**, alcoholic fermentation, V. 51a  
**Fusel oil** (see also Amyl alcohol), I. 178b, 360a; V. 403a  
 —, detn. of EtOH and H<sub>2</sub>O m., V. 408a  
 —, effect of yeast species on composition, V. 407c  
 — in lacquers, II. 409a  
 —, potato and corn, V. 406a  
 —, removal from spirits, V. 407a  
 —, separation of alcohols in, V. 407d  
 —, synthetic (see also Acetone); Butyl alcohol, II. 171d; V. 407b  
**Fusible** metals, I. 608a  
**Fustic**, IV. 126b  
**Fustin, VI. 88b**  
**Fuze** powder, IV. 159b  
 —, safety, IV. 459b

G

- G-Acid**, IV. 209d  
 **$\gamma$ -Acid**, IV. 209d  
**Gabbro, V. 408b**  
**Gadolin** reaction, II. 376a  
**Gadoleic acid**, III. 247b  
**isoGadoleic acid** in chaulmoogra oil, II. 522d  
**Gadolinite, V. 411b**  
**Gadolinite**, II. 512b; IV. 245c, 321c; V. 409b  
**Gadolinium**, II. 511c; V. 409c  
 — acetylacetone, V. 412d  
 —, acid selenite, V. 412b  
 —, carbonate, V. 412c  
 —, complex cyanides, V. 412d  
 —, dimethyl phosphate, V. 412c  
 —, formate, V. 412c  
 —, halides, V. 411c  
 —, nitrate, V. 412b  
 —, organic salts, V. 412c  
 —, orthophosphate, V. 412b  
 —, oxalate, V. 412c  
 —, oxide and hydroxide, V. 411b  
 —, platinocyanide, V. 412d

- Gadolinium** potassium chromates, V. 412b  
 — salts, fractional separations, V. 410a  
 — of halogen oxy-acids, V. 411d  
 — selenate, V. 412a  
 — sulphate, V. 411d  
 — sulphide, V. 412a  
 — sulphite, V. 412a  
**Gadus** spp., III. 244c  
**Gartneria vaginata**, III. 257b  
**Gahnite**, V. 413a  
**Gahnospinel**, V. 413a  
**Gaize**, II. 140b  
**"*α*-Galactan,"** VI. 201b  
**Galactan** — sulphuric acid ester, blood anticoagulant, II. 23d  
***d*-Galactin**, V. 510c  
**Galactocarlose**, V. 58a  
**Galactogen**, II. 302d  
**Galactose**, II. 282b, 286a, 506c  
 —, 2-amino-, III. 91d  
***β*-Galactosidase**, II. 290b  
**Galactoside**, VI. 82c  
**Galacturonic acid**, II. 297d  
**Galafatite**, V. 413b  
***l*-Galaheptose**, II. 286d  
**"Galalith,"** V. 413b  
**Galam-butter**, I. 654b  
**Galanga root**, V. 413b  
**Galangin**, V. 413d  
**Galaxite**, V. 414b  
**Galbanum**, V. 414b  
 — oil, II. 188d  
 —, presence of cadinol in, II. 190b  
**Galbaresinic acid**, V. 414c  
***Galega officinalis***, V. 414d; VI. 88b  
**Galgine**, V. 414d  
**Galena**, II. 25b; V. 415a  
**Galiosin**, V. 416a  
***Galipea officinalis***, III. 462b  
**Galpine**, III. 462d  
**Galpoidine**, III. 462d, 463a  
**Galpoline**, III. 462d, 463a  
**Galpot**, V. 415c  
**Gallium and *G. spp.***, I. 516d; V. 415c  
***Galla B.P.***, V. 425a  
**Gallacetophenone**, V. 417a; VI. 400a  
**Gallie acid**, IV. 277b; V. 417a  
 —, detection and detn., III. 558d; V. 418a  
 —, dyes from, V. 418a  
 —, fermentation, V. 59a  
 —, oxidation, V. 417c  
 —, qualitative reactions, II. 570c  
 —, salts, V. 418c  
**Gallisin**, II. 290a  
**Gallium**, V. 418c  
 — acetate, V. 422c  
 — acetylacetone, V. 422a  
 — alloys, V. 419c  
 — "alums," V. 421d  
 — chlorate, V. 420d  
 —, crystal structure, V. 419b  
 —, detn., gravimetric, II. 592d  
 —, volumetric, II. 657b  
 — dibromide, V. 420d  
 — dichloride, V. 420b  
 — di-iodide, V. 420d  
 — ferrocyanide, V. 422c  
 — halides, V. 419d  
 — hydroxide, V. 421b  
 — iodate, V. 420d  
**Gallium monochloride**, V. 420c  
 — monoxide, V. 421a  
 — nitrate, V. 422a  
 — nitride, V. 422a  
 —, organic salts, V. 422c  
 — oxyiodate, V. 420d  
 — perchlorate, V. 420d  
 — phosphates, V. 422b  
 — phosphide, V. 422b  
 —, properties and spectra, V. 419a  
 —, qualitative reactions, II. 555c, 560d, 568a  
 — selenate, V. 422a  
 — sesquioxide, V. 421a  
 — silicotungstate, V. 422c  
 — suboxide, V. 421b  
 — sulphates, V. 421d  
 — sulphides, V. 421c  
 — thermometers, V. 419d  
 — trialkyl and triaryl, V. 422a  
 — tribromide, V. 420c  
 — trichloride, V. 420a  
 — trifluoride, V. 419d  
 — tri-iodide, V. 420d  
**Gallicocatechin**, II. 438c  
**Gallicoyaniline**, I. 569b  
**Galloflavin**, V. 423b  
 —, structure, V. 424c  
**isoGalloflavin**, V. 423b  
 —, trimethyl-, V. 423c  
**"Gallogen," ("gallol")** V. 418c  
**Gallotannic acid**, V. 424d  
**Galls**, V. 424d  
 —, Aleppo, Turkey or Levant, V. 425b  
 —, bacterial plant, V. 420c  
 —, crown-, V. 126d  
 —, plant, caused by chemicals, V. 427a  
 —, cedar-apple rust fungi, V. 427a  
 —, insects producing, V. 425a  
***Gallus domesticus***, IV. 253d  
**Galuteolin**, V. 427b; VI. 88b  
**Galvanised iron**, III. 397c; V. 427b  
 —, electro-, IV. 267a  
**"Galvene,"** III. 77a  
**Gamabufogenin**, II. 388b  
**Gamabufotoxin**, II. 388b  
**Gambier or Gambier catechu**, II. 433b  
 —, cube, II. 433b  
**Gambine H**, IV. 10a  
**Gamboge**, II. 188c, 237a; V. 427c  
**Gamabufogenin**, II. 388b  
**Gamabufotoxin**, II. 388b  
**Gamma acid**, IV. 209d  
**"Gandakaki,"** I. 490a  
**Gangue modifiers**, V. 265d, 266a  
**Ganister**, V. 427d  
**"Ganister, bastard,"** V. 428a  
**Garancine**, II. 74c, 524d  
**Garbage fats**, V. 428a  
 —, reduction processes, V. 428b  
***Garcinia* spp.**, I. 654b; II. 237a; IV. 56b; V. 380a, 427c  
**Garcinin, garcinol**, V. 380a  
**"Gardenal,"** I. 623a  
***Gardenia grandiflora*, *G. spp.***, V. 428c  
**Gardenic acid**, V. 428d  
**Gardenin**, V. 428d  
**Gardeniol**, V. 428d  
**Garlic**, V. 429a  
 — oil, I. 250b; V. 429b  
**Garnet**, I. 4c; V. 429b  
 — paper, V. 429d  
**Garnierite**, V. 429d  
**Gas**, air, V. 430a  
 — analysis, II. 674d  
 —, density method, II. 686c  
 —, fractional condensation, II. 685d  
 —, physical methods, II. 685d  
 —, Raman spectra, II. 687c  
 —, refractivity method, II. 687b  
 —, spectroscopic, absorption spectra, II. 687c  
 —, emission spectra, II. 687b  
 —, thermal conductivity method, II. 686d  
 —, viscosity method, II. 687a  
 —, blast-furnace, II. 345a; V. 376b  
 —, Blau, II. 3b  
 —, bleaching of wool, II. 16c  
 —, blue cross, II. 25a; III. 11c, 14b  
 —, —, shell, III. 1  
 —, water, II. 345a; V. 489b  
 —, bottle, V. 480b  
 —, burners, characteristics, V. 246d  
 —, carburetted water, II. 345a  
**Gas**, coal (*see also* Carbonisation; Coal carbonisation), V. 430d  
 —, ammonia recovery from, indirect process, V. 459a, 461a  
 —, and by-products, yields, V. 468d  
 —, benzole extraction from, in oil-washers, V. 464c  
 —, —, with activated carbon, III. 279d; V. 465c  
 —, —, silica gel, III. 270d  
 —, calorimetry, recording apparatus, V. 476d  
 —, combustion, "Oft number," V. 479c  
 —, tests, V. 479b  
 —, composition, V. 453a, 469a  
 —, condensation of hot, V. 453b  
 —, detection of hydrogen sulphide in, V. 478c  
 —, detn. of constituents, II. 674d, 681c; V. 478d  
 —, —, total sulphur, V. 478b  
 —, drying, V. 467d  
 —, from retorts and ovens, comparison, V. 453a  
 —, hot treatment, V. 446d  
 —, generation of hydrogen sulphide in gas holders, V. 468c  
 —, gum formation in, V. 468a  
 —, history, V. 430d  
 —, holders, V. 473d  
 —, iron carbonyl in, II. 357b  
 —, legislation, V. 439a  
 —, manufacture, disposal of effluents, V. 461c  
 —, exhausters in, V. 457b



- Gas**, coal, manufacture, waste heat boilers in, V. 441b  
 —, —, purification from cyanogen compounds, V. 466d  
 —, —, —, hydrogen sulphide, V. 461c, 467a  
 —, —, —, naphthalene, V. 454d, 464a  
 —, —, —, organic sulphur compounds, V. 465d  
 —, —, —, purifiers, V. 461c  
 —, —, —, retort connections and mains, V. 447a, 453b  
 —, —, —, setting, operation, V. 440d  
 —, —, —, tar fog extraction, V. 458c  
 —, —, —, valuation, "hydrocarbon enrichment value," V. 460a  
**Gas coal**, bituminous, V. 437b  
 —, —, brown coal or lignite, V. 437b  
 —, —, —, cannel, V. 437c  
 —, —, —, classification, V. 342, 437d  
 —, —, —, valuation, V. 437d  
 —, —, —, defence, *see* Chemical warfare defence.  
**Gases**, adsorption by charcoal, I. 148c, 150a; II. 317b  
 —, —, —, inert, detection and detn., II. 579b, 681d  
 —, —, —, toxic, respirators for, III. 18b  
 —, —, —, war, bibliography, III. 17b  
 —, —, —, blistering, lachrymatory, lethal, irritant and prickling, *see* Chemical warfare.  
 —, —, —, —, tear, *see* Gases, war, lachrymatory.  
 —, —, —, —, vesicant, *see* Gases, war, blistering.  
**Gas**, liquefied hydrocarbon, II. 3b; V. 480b  
 —, —, —, liquor and its distillation, I. 342d, 344d  
 —, —, —, mantles, V. 431c, 481d  
 —, —, —, artificial silk, V. 483d  
 —, —, —, cause of luminosity, V. 488a  
 —, —, —, "lighting fluid," V. 484d  
 —, —, —, ramie, V. 483b  
 —, —, —, self-lighting, V. 487d  
 —, —, —, spiderless, V. 487d  
 —, —, —, Welsbach, V. 482b  
 —, —, —, masks, III. 18b  
 —, —, —, natural, "stripping," V. 480c  
 —, —, —, oil, gaseous fuels from, II. 3b  
**Gasoline** recovery, II. 319c  
**Gaspacolor** photography, II. 446a  
**Gas**, perfect, definition, VI. 412a, 413d  
 —, —, —, poison, *see* Gas warfare.  
 —, —, —, prickling, III. 7d  
 —, —, —, producer, *see* Producer-gas.  
 —, —, —, suction, *see* Suction gas.  
**Gastrolabium calycinum**, III. 537d  
**Gas warfare**, III. 7b  
 —, —, —, defence, III. 18a  
 —, —, —, warming, V. 480d  
 —, —, —, water (*see also* Carburetted water gas; Coke manufacture; Fuel; Gas, coal), II. 345a; V. 489a  
 —, —, —, air-steam ratio in producing, V. 497a  
**Gas**, water, automatic valves for, V. 491b, 491c  
 —, —, —, blue, II. 345a  
 —, —, —, carburetted, *see* Carburetted water gas.  
 —, —, —, continuous production, V. 501b  
 —, —, —, equilibrium, V. 308c, 495d; VI. 209c, 318c, 325c  
 —, —, —, generator, V. 490c  
 —, —, —, reaction in, V. 495c; VI. 325c  
 —, —, —, history, V. 489a  
 —, —, —, operation cycle, V. 497d  
 —, —, —, of plant, V. 491d  
 —, —, —, plant and process, I. 334c; II. 315a; V. 489a; VI. 325c  
 —, —, —, production of hydrogen from, I. 331c; II. 423d; V. 502d; VI. 325c  
 —, —, —, reactions in producing, V. 495c  
 —, —, —, works products, analysis, III. 511d  
**Gattermann** reaction, II. 370a; III. 585d  
**Gauging** of cements, II. 136d  
 "Gauging plaster," II. 132d  
*Gaultheria procumbens*, *G. spp.*, V. 503c; VI. 92a  
**Gaultherin**, I. 692b; V. 503c; VI. 92a  
**Gaultherioside**, V. 503c; VI. 88b  
**Gauss** electrolytic cell, III. 51d  
**Gay Lussac's law**, VI. 412b  
**Gease**, IV. 314b, 394d  
**Geddic acid**, VI. 150b  
**Gedrite**, I. 302d  
**Gegenions**, III. 284a, 285d  
**Gehlenite**, II. 146d, 228a  
**Geijerene**, V. 503c  
**Gein** (geoside), IV. 394d; VI. 88c  
 —, —, vicianose in, II. 300b  
**Geissospermine**, V. 503d  
*Geissospermum vellosii*, alkaloid V. 503b  
**Gelatin** (*see also* Glue and glue testing), V. 504b  
 —, —, —, amino-acids, contents, V. 506b  
 —, —, —, analysis, V. 509a  
 —, —, —, as protective colloid, III. 287a  
 —, —, —, bichromated, II. 452d, V. 506c  
 —, —, —, bone, V. 505b  
 —, —, —, detn. in paper, V. 506c  
 —, —, —, dynamites, IV. 241c  
 —, —, —, fluid, I. 293d; V. 269c  
 —, —, —, gels, III. 291a; V. 507b  
 —, —, —, gold number, III. 287c  
 —, —, —, hydrolysis and quality, V. 500d  
 —, —, —, in photographic film, II. 448a  
**Gelatinising** agents for smokeless powders, IV. 523c  
**Gelatin**, isoelectric point and properties, V. 505c  
 —, —, —, photographic, V. 508c  
 —, —, —, physical tests, V. 508c  
**Gelatins A and B**, V. 505d  
 —, —, —, hide and skin, V. 504b  
**Gelatin** solutions,  $p_H$ , V. 500b, 509b  
 —, —, —, viscosity, V. 508a  
 —, —, —, sulphur dioxide in, detn., V. 305b, 509c  
**Gelatin**, uses, II. 28b  
**Gelation** hysteresis, III. 291b  
 "Gelnigite," IV. 212a  
**Gelose**, V. 510c  
**Gels** and gelation, III. 291a; V. 507b  
**Gelsemic acid** and gelsemine, V. 510c  
**Gelseminine** and gelseminine, V. 510c  
**Gelsemine**, V. 510c  
**Gelsemium**, alkaloids, V. 510c  
**Gelsemoidine**, V. 510d  
 "Gelsa," I. 90c, 94d  
**Gems**, artificial, V. 511c, 605d  
**Gemsbok** beans, V. 514c  
**Gems**, doublet and triplet, V. 513d  
 —, —, —, imitation and counterfeit, V. 513b  
**Geneserine**, II. 199d  
**Geneva**, V. 532b  
**Genins**, II. 381b  
*Genista tinctoria*, IV. 180a; VI. 88c  
**Genistein**, genistin, IV. 189a, d; V. 259d; VI. 88c  
**Genkwanin**, V. 514b  
**Genthite**, V. 430a  
**Gentiagenin**, V. 515b  
**Gentiamarin**, V. 515b  
**Gentian**, V. 515a  
*Gentiana lutea*, *G. spp.*, III. 551c; V. 515a, 516a  
**Gentianin**, III. 551c; V. 516a  
**Gentianose**, II. 282b, 301a; V. 515d  
**Genticaulin**, primeverose in, II. 300b  
**Gentiin**, V. 515b  
**Gentiobiase**, II. 442c  
**Gentiobiose**, I. 357d; II. 298b, 299b, 442c; V. 516a  
**Gentiopiecin**, V. 515b  
**Gentisin**, V. 516b  
**Gentisic acid**, V. 53a; VI. 202a  
**Gentisin**, V. 515d, 516b  
**Genkwanin**, V. 514b  
**Geocoronium**, I. 539a  
**Geodin**, V. 58b  
**Geoffroyine**, V. 517a  
 "Geoform," VI. 141a  
**Geoside** (gein), VI. 88c  
**Geosol**, IV. 394d; VI. 140d  
 "Geosote," antiseptic, IV. 28b  
**Geranial**, III. 183d  
**Geranic acid**, III. 184a; V. 517b  
**Geranicol**, V. 517a  
**Geraniolene**, V. 518d  
**Geraniol** in perfumes, V. 518b  
 —, —, —, occurrence, II. 249c; III. 183c, 191a  
 —, —, —, reduction, II. 426d  
*cycloGeraniols*, V. 517c  
**Geranium** (artificial), V. 519a  
 —, —, —, essential oil, V. 519a  
 —, —, —, oil, Indian, V. 519c  
 —, —, —, Turkish, V. 517a, 519c  
**Geranyl** esters and Me ether, V. 518c  
 —, —, —, glucoside, VI. 88c  
 "German alloy," I. 253a  
**Germanam**, V. 525c  
**Germanates**, thio-, and esters, V. 525b  
**Germane**, mono-, chlorine derivs., V. 522c  
 —, —, —, triphenyl-, V. 526c

- Germanic acids**, ortho- and meta-, V. 524<sup>c</sup>  
 — nitride, ethyl-, V. 526b  
 — oxide and allotropes, V. 524a  
 — —, ethyl-, V. 526b  
 — sulphate, V. 525b  
 — sulphide, V. 525a
- Germanide**, sodium triphenyl-, V. 526<sup>c</sup>
- Germanite**, V. 519<sup>c</sup>
- Germanium**, V. 520<sup>c</sup>  
 — alkyls, V. 525d  
 — alloys, V. 521b  
 — aryl deriva., V. 526b  
 — bisacetylacetone dichloride, V. 527<sup>c</sup>  
 — bromide, ethylisopropyl-phenyl-, V. 527b  
 — —, triethyl-, V. 526a  
 —, detn., II. 595b  
 — di- and tetra-halides, V. 522d, 523b  
 — dibromide, diethyl-, V. 526a  
 — —, diphenyl-, V. 526d  
 — dihydride, V. 522a  
 — diphenyl, V. 527b  
 — fluorides, V. 522b  
 — hydrides, mono-, di-, and tri-germane, V. 521d  
 — inides, V. 525<sup>c</sup>  
 —, qualitative reactions, II. 553a, 558a, 571a  
 — tetrahydride, V. 521d  
 — tetraphenyl, V. 526b  
 — tri-iodide, ethyl-, V. 526b
- Germanochloroform**, V. 522<sup>c</sup>
- Germanol**, triphenyl-, V. 526d
- Germanomethane**, V. 521d
- Germanopropane**, octa-phenyl-, V. 527a
- Germanous oxide**, V. 523d  
 — sulphide, V. 525a
- German silver**, V. 519<sup>c</sup>
- Germerine**, VI. 200d
- Gersdorffite**, I. 469a; V. 529<sup>c</sup>
- Gesnerin**, V. 529d
- Getah wax**, V. 171a
- Geum urbanum**, gem from, IV. 394d
- Geyserite**, V. 530b
- Ghedda**, V. 530b
- Ghee**, II. 168<sup>c</sup>; V. 530b  
 — "Ghee, vegetable," V. 531d
- Gialloino**, V. 531d
- Giant ion**, III. 284<sup>c</sup>
- Gibb's adsorption isotherm**, III. 282b; IV. 284d
- Gibbs electrolytic cell**, III. 53a
- Gibbsite**, I. 284b; V. 532a
- Gilsonite**, V. 532a
- Gin**, V. 532b  
 —, adulteration, V. 533a
- Gingelly oil**, *see* Sesame oil.
- Ginger**, V. 533b  
 —, adulteration, V. 535b  
 — beer, I. 158b  
 —, essential oil, V. 535d
- Gingergrass**, essential oil, V. 536<sup>a</sup>
- Gingerol**, V. 533d  
 — "Ginger, wild," I. 496d
- Gingill oil**, *see* Sesame oil.
- Ginkgo**, V. 536a
- Ginkgoain** and ginkgol, V. 536a
- Ginning**, cotton, II. 401b
- Girard's reagents**, V. 536b
- Girolé**, I. 577a
- Gitalin**, II. 384a
- Gitonin**, II. 384a; VI. 88d
- Gitoxigenin**, II. 382a
- Gitoxin**, II. 381a; VI. 88d
- Gladstone and Dale's formula**, V. 546b
- Glaserite**, I. 450b
- Glaser method**, V. 78<sup>c</sup>
- Glass**, I. 559d; V. 536d  
 —, absorption and transmission of light by, V. 546d, 547d  
 — — air surfaces, reflection at, loss of light by, V. 551b  
 — ampoules, B.P. test, V. 539d  
 — annealing kilns and lehrs, V. 596a, 597  
 — —, range, V. 595<sup>c</sup>  
 — beads, V. 605<sup>c</sup>  
 —, best crystal, V. 561<sup>c</sup>  
 —, birefringence under stress, V. 595b  
 —, black, V. 564d  
 — blowing machine, Owen's, V. 581<sup>c</sup>  
 —, borosilicate, II. 51a  
 — building-bricks, V. 595a  
 — chemical, V. 561<sup>c</sup>  
 —, cohesion (temperature, V. 541d  
 —, coloured, V. 558a  
 — — by colloidal Au, Cu or Se, V. 558a  
 —, colouring, with chromium, V. 561d  
 — —, — cobalt, V. 561<sup>c</sup>; 565a  
 — —, — copper, V. 561d, 564d  
 — —, — manganese, V. 561d, 565a  
 — —, — nickel, V. 562a  
 — —, — selenium, V. 562a, 561d  
 — —, — uranium, V. 561d, 565a  
 — compound, V. 596<sup>c</sup>  
 —, compressibility, V. 551b  
 — constituents, properties of silica and its compounds, V. 577  
 —, copper films on, V. 603d  
 —, decolorising, chemical and physical methods, V. 574a  
 —, decoration, bevelling, V. 600<sup>c</sup>  
 — —, casing, V. 599d  
 — —, cutting, V. 600a  
 — —, engraving, V. 600b  
 — —, etching, V. 281<sup>c</sup>, 600<sup>c</sup>  
 — —, sandblasting, V. 601b  
 — —, sculpture, V. 600<sup>c</sup>  
 —, definition, V. 537d  
 —, devitrification, V. 575a  
 —, dielectric constant, V. 553a  
 — —, loss in, V. 553a  
 — —, strength, V. 553b  
 —, dispersion and refraction, V. 544a, 546a  
 — drawing machine, Ford's, V. 594a  
 — — —, Fourcault's and Pittsburgh's, V. 591<sup>c</sup>  
 —, durability, powder test, V. 539a  
 — —, tests for, V. 539<sup>c</sup>  
 —, elastic after-working effect in, V. 551b  
 — —, properties, V. 553b  
 —, electrical conductivity, V. 552b  
 —, enamelling, V. 605a  
 —, Glasses, coloured, infra-red transmission, V. 549b  
 — —, visual transmission, V. 549a, 550b
- Glasses**, lead-containing, V. 556<sup>c</sup>  
 —, lime-soda, common, V. 556a  
 —, organic safety, V. 609d  
 —, safety, laminated, V. 609b  
 —, solarisation effect on ultra-violet transmission, V. 551b  
 —, ultra-violet transmission, V. 551<sup>c</sup>
- Glass**, evaporated metal films on, V. 604b  
 — furnace, Cornelius, V. 571<sup>c</sup>  
 — grinding and polishing machines, V. 596d, 598, 599  
 —, hardening, V. 596b, 608d  
 —, heat-resisting, V. 557b  
 —, impact strength, V. 555b  
 —, iridescent, V. 604<sup>c</sup>  
 —, lampworking, V. 557a  
 —, lustres, V. 604<sup>c</sup>
- Glassmaking**, blowing and pressing machines, V. 582<sup>c</sup>  
 —, pot furnaces for, V. 567a  
 —, "Pyrobor" in, V. 559d  
 —, rasorite in, V. 559d  
 —, raw materials for, V. 558<sup>c</sup>  
 —, refractory materials in, V. 565<sup>c</sup>  
 —, silica for, V. 558<sup>c</sup>  
 —, tank furnaces for, V. 507d
- Glass manufacture**, batches in, V. 562  
 — melting furnaces, electric, V. 570d  
 — — process, V. 573b  
 — —, cullet in, V. 573d  
 — —, moisture effect, V. 574a  
 — —, progress of reaction, V. 572b  
 — —, stages in, V. 573b  
 — —, volatilisation in, V. 572a
- "Glass of antimony," I. 443b, 447b
- Glass**, opal, production, V. 558b, 561<sup>c</sup>, 561d  
 —, optical, V. 606<sup>c</sup>  
 — —, properties, V. 546a  
 — —, painting, V. 605b  
 —, plate and window, V. 556b  
 —, Poisson's ratio, V. 554b  
 —, powdered abrasive, I. 4<sup>c</sup>  
 —, properties, V. 538a  
 —, red, copper ruby, V. 564d  
 — —, gold ruby, V. 564d  
 —, refractive index, V. 544a, 546a  
 —, reinforced, V. 608b  
 —, safety, V. 608b  
 —, silvering, V. 603a  
 —, "softening point," V. 542a  
 —, specific heat, V. 543d  
 —, — volume or density, V. 542b  
 —, spectral transmission, effect of temperature on, V. 547, 548  
 —, sprayed metal films on, V. 604b  
 —, sputtered films on, V. 604b  
 —, staining, V. 604d  
 —, strain, annealing, V. 595b  
 — — viewed in polarised light, V. 596a  
 —, strength, effect of conditions on, V. 554<sup>c</sup>, 555a  
 —, stress-optical properties, V. 546<sup>c</sup>

**Glass**, surface tension, V. 542b  
 --, thermal after-working effect in, V. 554c  
 --, -- conductivity, V. 545a  
 --, -- endurance, V. 545a  
 --, -- expansion, V. 543a  
 "Glass, *Thermolux*," V. 595a  
**Glass** thread and wool manufacture, V. 591b  
 --, toughened\* V. 596b, 608b  
 -- tube machine, Danner's V. 589  
 -- tubing manufacture, V. 581b  
 --, viscosity, V. 541a  
 --, visual transmission, V. 550b  
**Glassware**, chemical, general scientific and heat-resisting, V. 556d  
 --, illuminating, V. 556b  
 --, manufacture, V. 578c  
 --, melting off and cracking off machines, V. 602b  
 --, pressed, V. 556b  
**Glass**, Young's modulus, V. 553c  
**Glauberite**, II. 233c  
**Glaucanic acid**, V. 56b  
**Glaucetrine**, VI. 1d  
**Glaucic acid**, V. 56b  
**Glaucidine**, VI. 1c  
**Glaucine**, VI. 1a  
**Glaucobilin**, I. 691c  
**Glauconic acid**, V. 56b  
**Glaconite**, VI. 1d  
**Glaze**, crystalline, VI. 11b  
 --, dry, VI. 2d  
 --, granite, VI. 9a  
 --, jet, and Majolica, VI. 8c  
 --, red, VI. 12a  
 --, Rouge Flambe, VI. 12a  
 --, salt, VI. 3d  
**Glazes and frits**, VI. 2c  
 --, craquelé, VI. 11d  
 --, decorative, 11a  
 --, lead, VI. 8a  
 --, leadless, VI. 9c  
 --, slip, VI. 9d  
**Glessite**, I. 302d  
**Gladin**, II. 85a, 505a  
 --, glutenn ratio, II. 84c, 505b  
 -- in flour, II. 74d, 84c, 85a  
 --, -- gluten, II. 84c, 501c, 505a  
**Gliadins**, rice, II. 493b  
**Glimmerton**, III. 196c  
 "Globak," II. 480a  
**Globin**, sepn. from haematin, VI. 161b  
**Globulin** in blood serum, II. 19d  
**Globulins**, VI. 13b  
**Globulol**, VI. 13b  
**Glonoine oil**, IV. 491d  
**Gloriosine**, III. 276c  
**Gloriosol**, VI. 93c  
**Glucal**, II. 291c  
*iso***Glucal**, II. 291c  
*β*-**Glucose**, II. 412c; IV. 282d  
**Glucinum**, *see* Beryllium.  
**Glucocheirolin**, VI. 88d, 91b  
**Glucoclhoral**, III. 35c  
**Glucoerythrose**, II. 298c  
**Glucogallin**, VI. 89a  
**Glucolysis**, VI. 74a  
**Glucanasturtin**, VI. 89a  
**Gluconic acid**, II. 285b, 297a; IV. 316a  
*d*-**Gluconic acid** from mould fermentation, V. 49c  
**Glucolactone**, II. 283b  
**Glucosamine** in chitin, III. 34b

**Glucosans**, II. 297b  
**Glucose** (dextrose), II. 282b, 281a, 289a  
 -- -azo dyes of catechol, II. 433b  
**Glucoseen-1:2**, II. 295a  
 -- -5:6, II. 291d  
**Glucose**, mutarotation, VI. 250a  
 --, oxidation by ceric salts, II. 510d  
 --, relation to cellulose, II. 457a  
 --, structure, II. 285b  
 -- units in polysaccharides, II. 301d  
**Glucosidase**, IV. 313b, 314b  
**Glucoside**, definition, VI. 82b  
**Glucosides**, *see* Glycosides.  
*β*-**Glucosido-gallio acid**, VI. 89a  
**Glucotropaeolin**, VI. 89a  
**Glucovanillin**, VI. 86b  
**Glucosylose**, II. 298b, 300c  
**Glucuronic acid**, II. 297d; VI. 21a  
**Glue**, adhesive strength, I. 142c; VI. 28b  
 and glue testing (*see also* Gelatin), VI. 21a  
 --, bone, manufacture, VI. 23a  
 --, casein, II. 114b  
 --, fish, VI. 25a  
 --, foam detn., VI. 29b  
 --, jelly strength, VI. 26d  
 --, liquid, Dumoulin's, V. 506a  
 --, melting point, VI. 27d  
 --, reaction, *p<sub>a</sub>* value, VI. 29c  
**Glues**, hide and skin, manufacture, VI. 21d  
**Glue size**, VI. 25b  
 --, sulphur dioxide content, VI. 29d  
 -- tensile strength measurement, VI. 28d  
 -- vegetable, III. 570d  
 --, viscosity test, VI. 27c  
 --, water absorption test, VI. 29a  
**Gluside**, IV. 28d  
 "Gluside," antiseptic action, IV. 28d  
**Glutaconic acid**, *cis*- and *trans*-, VI. 30b  
**Glutamic acid**, VI. 31d, 33a, 35d, 36b  
 -- as food, VI. 33c  
 --, *β*-hydroxy-, I. 318c; VI. 36d  
 --, --, detn., VI. 37a  
**Glutamine**, VI. 37b  
*d*-*iso***Glutamine**, VI. 38c  
**Glutaminic acid**, VI. 31d  
*γ* - **Glutamyl** - cysteinyl - glycine, III. 511a  
**Glutanic acid**, VI. 39a  
**Glutaric acid**, VI. 39a  
 --, alkyl derivs., VI. 39d  
 --, *α*-amino-, VI. 31d  
 --, methyl derivs., VI. 39d  
 --, prepn., II. 366a  
 -- acids, halogeno-, VI. 39c  
 --, *α*-hydroxy-, VI. 39a  
 -- acid, 1-trihydroxy-, I. 454a  
**Glutarmonoaldehyde**, VI. 34a  
**Glutathione**, III. 541a; IV. 311b  
**Gluten**, II. 85d  
 -- in malting, II. 88d  
**Gluten**, II. 84c  
 --, detn., II. 84c, 506a

**Glutenin**, II. 85b, 505a  
**Gluten** in baking, II. 74d, 77c, 84c, 504c  
**Glutenin** in flour, II. 74d, 84c, 85b, 505a  
 --, -- gluten, II. 84c  
**Gluten**, wheat, II. 504b  
**Glutimides**, VI. 38d  
**Glutin** (*see also* Gelatin), III. 94c  
 "Glutinosa," II. 480d  
 "Glutolin," II. 480a  
**Glyceraldehyde**, VI. 56b  
 -- ethylacetal, I. 30c  
**Glycerates**, VI. 50c  
**Glyceric acid**, VI. 40b  
**Glycerides** (*see also* Butter; Fats; Oils; and individual glycerides), VI. 61c  
 --, mixed and simple, VI. 40d  
 --, mono- and di-, preparation, VI. 65c  
 --, optical isomers, VI. 65a  
 --, polymerisation of unsaturated, IV. 89d  
 --, tri-, n.p., tables, VI. 66, 67, 68  
 --, --, double and triple melting points, VI. 66c, 67b  
**Glycerin** (*see also* Glycerol; Glyceryl), VI. 40c  
 --, analysis, detn. of glycols, VI. 63a  
 --, arsenic-free, VI. 40b  
 -- as preservative, V. 302c  
**Glycerinates**, VI. 56d  
**Glycerin**, candle crude, VI. 45d  
 -- cements and lutes, VI. 64c  
 --, C.P. or chemically pure, VI. 47a, 48a  
 --, crude, VI. 42b  
 --, distillation, VI. 42b, 46b  
 --, Twitchell, VI. 42b, 46a  
 --, detection and detn., V. 302d; VI. 57a  
 --, detn., acetin process, VI. 57c, 60b  
 --, --, copper process, VI. 57c  
 --, --, dichromate process, VI. 57b, 61c  
 --, --, micro-Zeiss, II. 634a  
 --, dynamile, VI. 47a, 48a  
**Glycerine**, *see* Glycerin.  
**Glycerin** evaporators, IV. 406a; VI. 43c  
 --, fermentation, II. 429b; V. 24d, 51b; VI. 41b, 46d  
 "Glycerin foots," VI. 70c  
**Glycerin**, industrial uses (*see also* "Alkyd" resins; Explosives; Food preservatives; Ink), II. 449b  
 -- production, II. 429b; VI. 41b  
 --, --, "refined," VI. 45d  
 --, saponification crude, VI. 42b, 45a  
**Glycerins**, crude, analysis, by International Standard methods, VI. 58d  
 --, distilled, VI. 47a  
**Glycerin**, soap lye and saponification crude, specifications, VI. 62c  
 --, -- or soap crude, VI. 42b, d  
 -- solutions, freezing-points, VI. 64b  
 -- stills, VI. 47b  
 --, synthetic, from propylene, VI. 41d  
 --, trinitro-, IV. 491c

- Glycerol**, *see also* Glycerides; Glycerin; Glyceryl-  
 — as solvent, VI. 55d  
 —, b.p. and vapour pressure of solutions, VI. 53b  
 — formins, V. 326b  
 —, alkyl-, V. 327a  
 — for nitroglycerin, IV. 491d  
 — from mould fermentation, V. 54b  
 —, nitric acid esters (*see also* Nitroglycerin), IV. 491a  
 —, properties, VI. 48c  
 —, refractive index of solutions, VI. 51, 52  
 —, sp.gr. and wt.-%, VI. 49, 50  
 —, sulphuric acid esters, VI. 69a  
 —, viscosities of solutions, VI. 54, 55  
**Glycerophosphoric acid** formation by yeast (*see also* Fermentation, alcoholic), II. 99d  
 **$\alpha$  - Glycerophosphoric acid** formation in muscle, VI. 76c  
**Glyceroxides**, *see* Glycerates.  
**Glycerylacetate**, I. 36c  
**Glyceryl arsenite**, VI. 69a  
 — borate, VI. 69b  
 — ether of guaiacol, VI. 140d  
 — ether,  $\alpha\beta$ -isopropylidene, VI. 70c  
 — ethers, diethyl and ditolyl, VI. 70c  
 — formate,  $\alpha$ - and  $\beta$ -, V. 326c  
 — mono-, di-, and tri-chlorohydrins, VI. 67d  
 —  $\alpha$ - and  $\beta$ -monophosphoric acid, VI. 69c  
 — phosphoric esters, VI. 69b  
 — phthalate, *see* "Alkyd" resins; "Glyptal" resins.  
 — tri- $\alpha$ -elaeostearate, IV. 258a  
 — trinitrate, *see* Nitroglycerin.  
**Glycidic acid**, VI. 71a  
 — esters, VI. 71b  
**Glycidol or glycide**, VI. 71c  
**Glycine**, VI. 71d  
 — anhydride, VI. 73a  
 — esters, VI. 72d  
**Glycine hispida**, I. 659c  
**Glycines**, aromatic, VI. 72d  
**Glycine**, tests for, VI. 73c  
 — "Glycobrom", VI. 73c  
**Glycocholic acid**, I. 689c  
**Glycoooll**, VI. 71d  
**Glycocolaminocarboxylic acid esters**, VI. 73a  
**Glycocololate**, heptanolmercuric, VI. 73a  
**Glycoooll**, oxidation, II. 278b  
**Glycooxyamine**, VI. 73c  
**Glycogen**, I. 1b; II. 282a, 302a, d  
 — from yeast, V. 13a  
**Glycogenase**, V. 14c  
**Glycogen** breakdown in muscle extract, VI. 77c  
**Glycol** (*see also under* Ethylene), IV. 377b  
 — acetate, IV. 383b  
 — carbonate, IV. 378a  
 — chlorohydrin, IV. 375b  
 — ethers, IV. 378b  
**Glycollic acid**, V. 73c  
**Glycol**, manufacture for explosives, IV. 490c  
 — monoethyl ether, IV. 378c  
 — ozonate, IV. 378a  
**gem-Glycols**, dialkyl ethers, I. 33d  
**Glycol vinyl ether**, I. 91c  
**Glycolysis** (*see also* Fermentation, alcoholic), I. 557c; VI. 73d  
 —, activators and inhibitors, VI. 81b, 82a  
 —, aerobic, VI. 80c  
 —, anaerobic, of tissues *in vitro*, VI. 80a  
 —, blood, VI. 74b  
 —, —, and clotting, II. 22d  
 —, co-enzyme in, VI. 78c  
 —, effect of lack of oxygen and glucose, VI. 81c  
 —, —, fluoride, VI. 81d  
 —, —, glyceraldehyde, VI. 82a  
 —, —, iodoacetic acid, VI. 81c  
 —, —, — K and Ca ions, VI. 81b  
 —, —, phloridzin, VI. 81d  
 — in brain, VI. 76b  
 — muscle, VI. 74d  
 — tumours, VI. 80b  
 —, methylglyoxal in, VI. 78d  
 — of sugars, VI. 82a  
 —, pyruvic acid in, VI. 81b  
 — "Glycosal", VI. 82b  
**Glycosides**, VI. 82b  
 —, biological significance, VI. 85a  
 —, cyanophoric (*see also* Amygdalin; Emulsin), III. 531b  
 —, disaccharides in, VI. 83a  
 —, enzymic synthesis, IV. 313d; VI. 84b  
 —, hydrolysis by enzymes (*see also* Enzymes), VI. 81c  
 —, natural, carbohydrates of, VI. 82d  
 —, nitrile, VI. 83d  
 —, phenolic, VI. 83b  
 —, purine and pyrimidine, VI. 83c  
 —, purpurea, A and B, II. 384a  
 —,  $\gamma$ -pyran derivs., VI. 83b  
 —, steroid, VI. 83c  
 —, sulphur compounds, VI. 83d  
 —, synthesis, VI. 83d  
**Glycoxide**, sodium, IV. 377d  
 **$\delta$ -Glycuronic acid**, I. 12a  
**Glycyl ethyl ester** glucoside, VI. 73b  
**Glycylglyceride**,  $\alpha$ -mono-, VI. 73b  
**Glycymerin**, II. 401d; VI. 98b  
**Glycyphyllin**, VI. 80a  
**Glycyrrhetic acid**, VI. 98b  
**Glycyrrhetin**, VI. 98b  
**Glycyrrhiza glabra** (*Radix liquiritiae*), VI. 91b  
**Glycyrrhizic acid**, detn., VI. 98c  
**Glyoxal**, I. 80b, 99c, 565c; VI. 98c  
**Glyoxalase**, VI. 78d  
**Glyoxaline**, VI. 98d  
 — 5-alanine, VI. 231c  
**Glyoxal sulphate**, I. 99c  
 — trimeride, VI. 98c  
**Glyoxime**, VI. 98d  
**Glyoxylic acid**, VI. 99c  
 —, condensation with urea, VI. 100b  
 —, detection, VI. 100c  
**Glyphenarsine**, I. 487b; VI. 100d  
**"Glyptal"** resins, I. 238c; II. 469a; VI. 64a  
 — in lacquers, II. 472d  
**Gmelinol**, VI. 100c  
**Gneiss**, II. 314c; VI. 126b  
**Gnoscopine**, VI. 100d  
**Goa powder**, I. 457b; III. 116b; VI. 100d  
**Goethite**, II. 25d; III. 386d; VI. 100d  
**Gold**, VI. 101c  
 — alloys, VI. 109c  
 — amalgams, VI. 110a  
 — carbide, II. 280b, 281b  
 —, colloidal, II. 410c; III. 287b; VI. 100b  
 — compounds (*see also* Auric, Aurosaureic, Aurous, Auryl compounds), VI. 110d  
 —, inorganic, containing complex organic radicals, VI. 118d  
 —, organic, VI. 119b  
 —, co-ordination compounds, VI. 111a  
 — copper alloys, VI. 109c  
 —, co-valency, VI. 111a, 121b  
 — cyanides, III. 486a; VI. 115a  
 —, detn., assay, I. 524c  
 —, electrodeposition, II. 701a  
 —, gravimetric, II. 587a  
 —, volumetric, II. 657b  
 —, diethylmonobromo-, and derivs., VI. 119c, 120a  
 —, electrodeposition, IV. 285a  
**Golden sulphide** of antimony, I. 447a  
 — wattle, I. 11c  
**Gold** extraction, "all-sliming" methods, VI. 105b  
 —, amalgamation, VI. 102c  
 — by flotation, VI. 107a  
 —, crushing by stamps, VI. 103a  
 —, cyanide process, III. 486b; VI. 102c, 104a, 115a  
 —, filtration of slime, VI. 105d  
 — from cyanide solutions, VI. 106a  
 — ores, VI. 102b  
 —, gravel washing, VI. 102b  
 —, gravity concentration, VI. 102c, 103d  
 —, Merrill-Crowe process, VI. 106c  
 — ore crushing, VI. 102c, 103b  
 —, separation of pulp, VI. 105a  
 —, slime treatment, VI. 105c  
 —, Taverner process, VI. 106c  
 —, tube mills, VI. 103b  
 —, Faraday's (*see also* Gold, colloidal), VI. 102b  
 — films from diethylmonobromogold, VI. 119d  
 — flux, I. 559c  
 —, fulminating, VI. 116c  
 — imido-compounds, complex, VI. 118c  
 — iron alloys, VI. 110a  
 — lace, VI. 110b  
 — leaf, VI. 110b, 110d  
 —, legal standards, VI. 110c  
 —, Mannheim, VI. 122a  
 — monobromo-, VI. 113c

- Gold**, monochloro-, VI. 113*d*  
 —, ammino-, VI. 114*a*  
 —, dibenzylsulphido-, VI. 114*a*  
 —, monocyanide, VI. 115*b*  
 —, monocyano-, diethyl, VI. 121*a*  
 —, moniodo-, VI. 114*d*  
 —, diethyl, VI. 120*b*  
 —, triethylphosphino-, VI. 114*d*  
 —, trimethylarsino-, VI. 114*d*  
 —, mosaic, VI. 122*a*  
 —, number, III. 287*b*  
 —, ore, classifiers of ground, VI. 103*c*  
 —, —, Dorr bowl classifier, VI. 103*d*  
 —, ores, VI. 101*d*  
 —, oxides, VI. 115*d*  
 —, parting by sulphuric acid, VI. 107*d*, 109*d*  
 —, placer deposits, VI. 102*a*  
 —, powders, II. 118*d*  
 —, precipitation, VI. 100*a*  
 —, properties, III. 287*b*; VI. 109*b*  
 —, purple, II. 410*c*; V. 513*c*; VI. 122*b*  
 —, pyridinotrichloro-, VI. 113*a*  
 —, qualitative reactions, II. 506*d*  
 —, —, rare metals present, II. 551*d*, 550*d*  
 —, refining, VI. 107*c*  
 —, —, by electrolytic deposition, VI. 108*a*  
 —, —, chlorine process, VI. 108*d*  
 —, —, Moebius process, VI. 108*a*  
 —, —, silver recovery from, VI. 108*a*  
 —, —, sulphuric acid process, VI. 107*d*  
 —, —, Wohlwill process, VI. 108*b*  
 —, salts, VI. 117*a*  
 —, silver alloys, VI. 107*d*, 109*d*  
 —, smelting, VI. 107*c*  
 —, solders, VI. 110*b*  
 —, soils, blue and red (*see also* Gold, colloidal), II. 280*c*  
 —, sulphides, VI. 110*b*  
 —, sulphides, complex, VI. 117*c*  
 —, sulpho-telluride ores, treatment with cyanide, VI. 106*d*  
 —, —, telluride, II. 201*c*  
 —, "Gold therapy," VI. 117*d*, 118*d*  
**Goldthioglucose**, VI. 119*a*  
**Gold toning** of silver prints, VI. 117*d*  
**Gold** (tribromide (tribromogold) VI. 111*b*  
 —, trichloride, co-ordination compounds, VI. 113*a*  
 —, trihydroxide, VI. 115*d*  
 —, uses, VI. 110*b*  
 —, wares, VI. 110*b*  
 —, —, colouring, VI. 110*c*  
 —, "Gomenol," VI. 123*a*  
 —, "Gommeline," I. 143*c*  
 —, "Gond babul," I. 585*a*, *b*  
**Gondang** wax, V. 171*b*; VI. 123*b*  
**Goniometer**, V. 123*b*  
**Gooseberry**, VI. 124*d*  
**Gorlic** acid, II. 523*b*  
**Gorli** (gorley) seed oil, II. 523*b*  
**Gorae**, VI. 125*a*  
 "Gosio gas," I. 479*d*, 483*c*  
**Goslarite**, VI. 125*b*  
**Gossypetin**, I. 161*c*; III. 405*b*  
**Gossypitone**, III. 405*d*  
**Gossypitrin**, III. 406*b*; VI. 89*b*  
**Gossypitrone**, III. 406*c*  
**Gossypium** spp., V. 130*b*  
**Gossypol**, apogossypol, III. 407*b*, 408*b*, 410*a*; IV. 252*b*  
**Goulard's** extract, lotion and water, I. 55*c*; VI. 125*c*  
 "Grahams salt," VI. 125*c*  
**Grains** of Paradise, I. 161*a*  
**Gramine**, VI. 125*c*, 403*c*  
**Granite**, V. 4*a*; VI. 126*a*  
 —, -aphte, III. 32*d*  
 "Granite, black," V. 409*a*; VI. 127*c*  
**Granite** building stone, II. 137*c*  
 —, graphc, VI. 126*b*  
 —, Mendip, Petd., II. 137*d*; VI. 127*c*  
 —, -pegmatite, III. 32*d*  
**Granulite**, VI. 126*a*  
**Granulobacter pectinovorum**, V. 150*c*  
**Grape**, VI. 127*d*  
 —, fruit, VI. 129*a*  
 —, —, essential oil, VI. 130*b*  
 —, —, pectin content, VI. 128*c*, 130*b*  
 —, "honey," VI. 128*c*  
 —, juice, methyl anthramlate m., VI. 128*c*  
 —, —, preservation, VI. 128*c*  
 —, seed oil, IV. 86*c*; VI. 130*c*  
 —, —, types, VI. 131*d*  
**Grapes**, ripening, VI. 128*b*  
**Graphic granite**, VI. 126*b*  
**Graphite** (*see also* Black lead), II. 300*a*, 313*d*  
**Graphitic acid**, II. 300*d*; VI. 132*a*  
**Graphitites**, II. 310*a*  
 "Grappiers," II. 135*b*  
**Grass-cakes**, rapid drying, IV. 590*a*  
 —, cloths, III. 32*b*  
 —, Moroccan, II. 482*d*  
 —, ensilage, VI. 133*d*  
 —, —, driers for, VI. 134*a*  
**Grasses**, III. 433*a*; VI. 134*c*  
**Grass**, Indian buffalo, II. 482*d*  
**Grassing** of linen, II. 11*c*  
**Grass land**, VI. 132*c*  
 —, —, intensive manuring and grazing, VI. 133*c*  
 —, —, lime deficiency, VI. 132*d*  
 —, —, phosphate deficiency, VI. 133*a*  
**Graupen**, I. 694*d*  
**Grau-spiessglanzerz**, I. 416*b*  
 "Grauocaine," I. 369*c*  
**Grease**, animal, VI. 135*b*  
 —, black, VI. 135*d*  
 —, brown, VI. 134*d*, 135*c*  
 —, coatings and slushing compounds, III. 394*d*  
 —, curriers', VI. 135*b*  
 —, extraction, VI. 135*a*  
 —, fuller's, VI. 135*c*  
 —, garbage, house or kitchen, V. 428*a*; VI. 134*d*  
 —, (lard-) oil, VI. 135*a*  
 —, —, melted stuff, VI. 134*d*  
 —, —, oleine, distilled, VI. 135*c*  
 —, packers', VI. 134*d*  
 —, packing-house, VI. 134*d*  
 —, recovered, VI. 135*c*  
**Greases**, VI. 134*c*  
 —, skin, VI. 135*b*  
 —, stuffing, VI. 135*b*  
**Grease**, stearins, VI. 135*a*  
 —, tankage, VI. 135*a*  
 —, whale, VI. 135*b*  
 —, white, VI. 134*d*  
 —, wool, VI. 135*c*  
 —, —, fat, VI. 135*c*  
 —, yellow, VI. 134*d*  
 —, Yorkshire, VI. 135*c*  
 "Greasy stone," I. 102*c*  
**Green**, Acid Alizarin B, BG, I. 393*b*, 393*c*, 230*c*  
 —, Aldehyde, I. 193*c*  
**Greenalite**, VI. 135*d*  
**Green**, Alizarin, I. 205*b*, 229*a*, 397*a*  
 —, Brilliant, G, SE, I. 232*a*  
 —, —, Cyanine, I. 232*a*  
 —, —, Cyanine I, I. 205*b*, 231*a*, 404*d*  
 —, Direct, G, I. 406*c*  
 —, Alsace, I. 263*a*  
 —, Anthraquinone, GX, I. 400*a*  
 —, Azine, GB, I. 572*d*, 570*a*  
 —, Baryta, I. 642*d*  
 —, Bindschedler's, VI. 418*a*  
 —, Brilliant, II. 105*b*  
 —, Brunswick, II. 119*b*; III. 112*d*, 350*b*  
 —, Caledon, 2B, BP, RC, I. 415*b*, 424*c*, 415*b*  
 —, Caledon Jade, I. 205*c*  
 —, —, G, 2G, 4G, X, I. 425*d*, 425*a*, 420*d*  
 —, Cassel, I. 642*d*; V. 297*d*  
 —, Casselmann's, II. 418*b*  
 —, Chrome, III. 107*b*, 112*d*  
 —, Chromium, III. 107*a*  
 —, Ciba, G, VI. 453*b*  
 —, Cibanone, B, I. 424*a*  
 —, Cobalt, III. 219*a*, *c*  
 —, earth, VI. 136*a*  
 —, ebony, VI. 136*b*  
 —, Emerald, I. 478*a*; III. 107*b*; IV. 279*c*  
 —, Guignet's, III. 107*b*; IV. 279*c*  
 —, Indanthrene Brilliant, FFB, I. 425*a*  
**Greenland** spar, III. 440*b*  
**Green**, Malachite, cryst., I. 425*d*  
 —, Manganoze, I. 642*d*  
**Greenockite**, II. 190*d*; VI. 136*d*  
**Green**, Pannetier's, III. 107*b*; IV. 279*c*  
 —, Paris, I. 478*a*  
 —, Prussian, III. 473*a*  
 —, Rinmann's, III. 219*a* <sup>2</sup>  
**Greens**, Acid, I. 120*a*  
**Greensand** in lime-exchange reactions, VI. 218*b*  
**Green**, Scheele's, I. 409*a*, 477*d*  
 —, Schweinfurt(h), I. 54*d*, 469*a*, 478*a*; IV. 279*c*  
 —, Soledon Jade, I. 429*b*  
 —, stone, IV. 8*a*, 53*b*  
 —, Turquoise, III. 219*b*  
 —, Ultramarine, III. 107*b*  
 —, Verdigris, I. 54*d*  
 —, Zinc, III. 113*d*  
**Grège**, V. 94*a*  
**Gränz-dextrins**, III. 568*b*  
**Grey** cloth and grey yarn, II. 3*d*; V. 151*d*  
 —, Indanthrene, K, I. 420*a*, *c*

- Grey**, Methylene, I. 500b  
**Greystone**, II. 133c  
**Griesheim** electrolytic cell, III. 50d  
**Grignard** compounds, luminescent oxidation, III. 23c  
 — reagent, VI. 137a  
 —, action on carbon dioxide, II. 363b  
 —, — ethyl carbonate, II. 363b  
 —, — metal chlorides, II. 357c  
 —, secondary reactants, VI. 137b  
**Grinding**, limits of fine, IV. 98a  
**Grieseofulvin**, V. 58c  
**Gri-shi-bu-ichi**, VI. 137c  
**Grisou** naphthalite-roche, IV. 474d  
 — tetrylite couche, IV. 487b  
**Grisoutine** couche and roche, IV. 553b  
**Grit**, I. 4b  
 —, building, II. 137d  
**Grog**, II. 520b; III. 100d; V. 568a  
**Grossular**, V. 429b  
**Grotthus-Draper** law, VI. 137d  
**Ground-nut**, I. 451c; VI. 138a  
 — oil, I. 454c  
**Growan**, III. 32c  
**Growth** factor or growth-promoting substances (*see also* Auxin; Heteroauxin), I. 558b; II. 98c; V. 420d; VI. 138b, 464a, 495c  
 "**Guacampol**," VI. 142b  
**Guaiacetin**, VI. 139a  
 "**Guaiachinol**," VI. 142b  
**Guaiacol**, II. 431b; VI. 139b  
 — acetate, II. 431d; IV. 392b  
 —, antiseptic properties, IV. 29c  
 —, azo-derivs., VI. 141d  
 —, cacodylate, II. 188b  
 —, carboxylic acid, VI. 141b  
 —, conversion into catechol, II. 430b  
 —, detection and detn., VI. 139d  
 — in pharmacy, VI. 139d  
 — urine, VI. 140b  
 — salol, VI. 140d  
 — sulphonic acid, alkali salts, VI. 140c  
 —, thio-, VI. 141d  
**Guaiacum officinale**, *G. sanctum*, VI. 142a  
**Guaiacum** resin, VI. 142a  
**Guaiacyl** acetate, VI. 141c  
 — benzoate, VI. 140c  
 — carbonate, VI. 141a  
 — chloroacetate, VI. 141c  
 — cinnamate, VI. 140d  
 — diethylaminoacetate, VI. 140d  
 — ethoxyacetate, VI. 141a  
 — glyceryl ether, VI. 140d  
 — phosphate, VI. 141d  
 — salicylate, VI. 140d  
 — succinate, VI. 140d  
 — thymyl carbonate, VI. 141b  
 — valerate, VI. 140d  
 — xanthate, thio-, VI. 141d  
 "**Guaiacform**," VI. 141a  
 "**Guaiakinol**," VI. 142b  
 "**Guaiamar**," VI. 140d, 142b  
**Guaiaretic acid**, VI. 142a  
 "**Guaiasanol**," VI. 140d  
**Guaiazulene**, I. 119d  
**Guaiene**, VI. 142c  
**Guaiol**, VI. 142b  
 — dihydroxy-oxide, VI. 142c  
**Guaiyl** acetate, VI. 142c  
**Guanamines**, VI. 147b  
**Guanase**, IV. 315a  
**Guanchi**, I. 4c  
 "**Guanicaine**," I. 120d  
**Guanidine**, VI. 142c  
 —, acetyl-, VI. 145d  
 —, alkyl and aryl derivs., VI. 146a  
 —, allylmalonyl-, VI. 146a  
 —, amino-, VI. 148d  
 —, —, condensation products, VI. 150a  
 —, —, detn., VI. 149b  
 —, bromo-, VI. 147b  
 —, chloro-, VI. 147b  
 — compounds with sugars, VI. 143d  
 —,  $\alpha$ -cyano-, VI. 147c  
 —, detection, VI. 144b, 146b  
 —, detn., colorimetric, VI. 143c, 144b  
 —, —, gravimetric, VI. 144c  
 —, diamino-, VI. 150b  
 —, formyl-, VI. 145d  
 — from ammonium thiocyanate, VI. 143a  
 —, nitro-, VI. 147c  
 —, nitroamino-, VI. 148c  
 —, nitro-, colour reactions, VI. 148a  
 —, nitroso-, VI. 148a  
 —, —, colour reactions, VI. 148b  
 —, prepn., VI. 142d  
 —, properties, VI. 143b  
 —, salts, VI. 146b  
**Guanidines**, separation from creatine and creatinine, VI. 144c  
**Guanidine**, Sullivan's test, VI. 144b  
 —, toxic properties, VI. 144a  
 —, triamino-, VI. 150b  
**Guanidino-glycylglycine**, VI. 146a  
 $\alpha$ -**Guanidinopropionic acid**, III. 416b  
**Guanine**, VI. 150c, 152a  
 —, acyl derivs., VI. 152c  
 —, azo-derivs., VI. 152c  
 —, bromo-, VI. 152d  
 —, deoxy-, VI. 152d  
 —, detection and detn., VI. 153a  
 —, mononucleotide, VI. 153a  
 —, physiological effects, VI. 151d  
 —, salts, VI. 152a  
**Guano**, V. 63c  
 —, bat, V. 64b  
 —, fish, V. 64b  
 —, meat, V. 66c  
 —, Peruvian, V. 63c  
 —, phosphatic, V. 80d  
**Guanosin** deamidase, IV. 315a  
**Guanosine**, IV. 322c; VI. 89b  
**Guanyl** azide, VI. 149d  
**Guanylic acid**, VI. 153a  
**Guanylnitrosoaminoguanyl-tetracene**, IV. 542d  
**Guara**, VI. 153b  
**Guarana**, VI. 153b  
 —, caffeine content, VI. 153c  
 —, theobromine in, II. 197c  
**Guareschi** reaction, II. 369a  
**"Guatannin"**, VI. 154a  
**Guava**, VI. 154a  
 — seed oil, VI. 154b  
**Gudmundite**, VI. 154d  
**"Guejarite"**, II. 518a  
**"Guhr"**, IV. 239b  
**Guinea** grains, I. 161a  
**Gulaman** dagat, VI. 154d  
**Guldberg** and Waage's law, *see* Mass action, law.  
**Gulose**, II. 286a  
**Gum**, acacia, I. 11d; VI. 155d  
 — Accroides, I. 12b  
 — arabic, I. 11d; VI. 155d  
 —, —, composition, VI. 155b  
 "**Gum**, Bengal," I. 585b  
**Gum** Benjamin, I. 615a  
 — benzoin, I. 615a  
 —, Botany Bay, I. 618a  
 — British, I. 143c; III. 570d  
 — Butca, II. 157d  
 — Cadie, II. 188c; V. 427c  
 — carot, VI. 156c  
 —, camalce or dekamalee, V. 428d  
 —, Dhak, III. 571a; VI. 435c  
 — formation in benzole (*see also* Gum inhibitors), I. 674a  
 — gedda, VI. 156b  
 —, ghatti, VI. 156a, 422c  
 —, Indian, VI. 422c  
 — inhibitors, I. 674a; VI. 469c  
 —, addition to fuels, VI. 182b  
 — and oxidation potentials, VI. 478a  
 —, colour stability, VI. 478c  
 —, hydrocarbon standard, VI. 477d  
 —, natural, VI. 481c  
 —, pretreatment of fuel, VI. 481b  
 — in motor fuel, tests for, VI. 471b  
 —, Kauri, II. 469d; III. 340a  
 —, locust, VI. 156c  
**Gumming** process, VI. 470b  
**Gummite**, VI. 154d  
 —, thoro-, VI. 155a  
 —, yttrio-, VI. 155a  
**Gum**, potential, detn., VI. 471d  
**Gums**, VI. 155a  
 —, constitution, VI. 155b  
 —, identification, VI. 156c  
 —, tragacanth, VI. 155c, 156a  
 —, varnish, VI. 155a  
 —, vegetable, I. 143c  
 —, viscosity, VI. 155c  
**Gunari**, II. 439d  
**Guncotton** (*see also* Nitrocellulose), IV. 501c, 512a  
 —, Abel's nitration process, IV. 508d  
 —, behaviour on heating and ignition, IV. 513a  
 —, boiling and pulping, IV. 510c  
 —, continuous nitration process, IV. 510b  
 —, dispersions, II. 459d  
 —, explosive properties, IV. 513b  
 — manufacture, purification and tests of cotton for, IV. 500b  
 —, moulded, IV. 511d  
 —, nitration by American process, IV. 510b  
 —, — dipping, IV. 509b  
 —, — displacement, IV. 509d

**Guncotton**, nitration in centrifuges, IV, 509c  
 —, testing and analysis, IV, 514b  
 —, washing, IV, 511d  
**Gunláh**, I, 4c  
**Gunpowder**, IV, 455a  
 —, analysis, IV, 162a  
 —, breaking down and pressing, IV, 457c  
 —, brown or cocoa, IV, 459a  
 —, density, IV, 160b, 462b  
 —, explosions, gases and pressures in, IV, 460b  
 —, granulating or corning, IV, 457d  
 —, grinding and incorporating, IV, 457a  
 —, hygrometric test, IV, 462c  
 —, pebble and persnatic, IV, 458d  
 —, sodium nitrate mixtures, IV, 463b  
 —, storing, finishing and blending, IV, 458b  
 —, sulphurless, IV, 463a  
**Gur-ginjá**, I, 4c  
**Gurjunenes**, VI, 156d  
 "Gutta," II, 119a  
**Gutta**, K, VI, 159b  
 —, para, VI, 159b  
 —, percha, VI, 157a  
 —, analyses, VI, 158c  
 —, from *Palagium spp.*, VI, 157b  
 —, — *Payena spp.*, VI, 157b  
 —, — golf balls, VI, 159b  
 —, in submarine cables, VI, 159a  
 —, substitutes, VI, 159b  
**Gutzeit's test**, I, 170b  
**Guvacine**, I, 458a, b  
**Guvacoline**, I, 458b  
**Guyacan**, VI, 159c  
**Gynergen**, IV, 330b  
**Gynocardia** oil, II, 522b  
**Gynocardin**, VI, 89b  
**Gynolactose**, I, 242a  
 "Gynoval," VI, 159c  
**Gypsogenin**, VI, 89c  
**Gypsophila-saponin**, VI, 89b  
**Gypsum**, II, 240a; VI, 159c  
 —, French, VI, 160a  
 —, in cellulose plastics, II, 171d  
 —, polishing tin-plate, VI, 160b  
 —, mineral, II, 129b  
 —, —, origin, VI, 160a  
 —, plasters, II, 129b  
 —, properties, II, 232b  
**Gyrolite**, II, 227c  
**Gyrophora spp.**, VI, 160c  
**Gyrophoric acid**, VI, 160c

H

**Haas-Oettel electrolytic cell**, III, 65d  
**Haber-Bosch process**, I, 335d  
**Hackberry-seed oil**, VI, 278d  
**Hackling** of linen, II, 11a  
**Hæm**, VI, 165c  
 "Hæmarogen," VI, 160b  
**Hæmatic acid**, I, 691b; III, 83b  
**Hæmatin**, VI, 161a, d  
 —, acid, VI, 161d  
 —, alkaline, VI, 161d  
 —, detection and detn., VI, 165b

**Hæmatin**, detn., spectroscopic, VI, 161c, 165b  
 —, histo- and myo-, III, 544a  
**Hæmatinic acid**, VI, 162b  
**Hæmatin** in catalase, II, 422c  
 —, — hæmoglobin, II, 20b  
 —, occurrence, VI, 165a  
 —, reactions, VI, 164c  
 —, reduced, VI, 165c  
**Hæmatins**, absorption spectrum, VI, 165b  
**Hæmatite**, II, 25a; VI, 160b  
 —, in carnallite, II, 390a  
**Hæmatogen**, II, 22a; VI, 160b  
 —, in antenna therapy, II, 22a  
**Hæmatoporphyrin**, II, 20c, 21a; VI, 161b  
 —, hydrobromide, dibromo-, VI, 161b  
**Hæmin**, II, 20c; VI, 161a  
 —, blood test, VI, 161b  
 —, synthesis, VI, 163a  
**Hæmochromogen**, VI, 161b, d, 165b  
 compounds of cytochrome, III, 511b  
**Hæmocyanin**, II, 20a  
**Hæmoglobin**, II, 20a; VI, 161b, 161c, 165c  
 —, carbon monoxide compound, II, 21c, 316a; VI, 166a, 167b  
 —, constitution, II, 20b; VI, 165c  
 in diet, II, 62b  
 —, invertebrate blood, VI, 165c  
 —, kinetics, VI, 167a  
 —, muscular, VI, 166d  
 —, oxidation, VI, 164d, 167b  
 —, oxygenation, VI, 164d, 165c, d, 166c  
**Hæmoglobins**, absorption spectrum, VI, 166a  
 "Hæmol," VI, 160b  
**Hæmophilia**, II, 22c  
 "Hæmopyrrole," II, 20c; III, 83b; VI, 162a  
**Hætnia**, VI, 169d  
**Hafnium**, II, 480b, 511c; VI, 169a  
 —, acetylaceton-, VI, 170c  
 boride, VI, 170c  
 carbide, II, 281d; VI, 170c  
 chlorides, VI, 170a  
 —, detn., see Zirconium, II, 537c  
 —, dioxide, VI, 169d  
 —, iodide, VI, 170b  
 —, nitrate, VI, 170b  
 —, oxybromide, VI, 170a  
 —, oxyfluoride, VI, 170a  
 —, phosphates, VI, 170b  
 —, qualitative reactions, II, 551a, 556b, d, 571d  
 —, separation from zirconium, VI, 169a  
 —, sulphate, VI, 170b  
 —, tetrafluoride, VI, 169d  
**Hafnyl chloride**, VI, 170a  
 —, phosphate, VI, 170b  
**Haglund process**, I, 268b  
**Haidingerite**, II, 226b  
**Hair dyeing**, VI, 171c  
 —, dyes (human), VI, 170c  
 —, salt, I, 280a  
 "Halarsol," I, 489b  
 "Halazone," IV, 20c  
**Halberg-Beth dry gas-clean ing**, V, 377

**Haldane apparatus**, II, 677a  
**Half value period**, VI, 172d, 173a  
**Halibut-liver oil**, vitamins, III, 250a  
**Halides**, see also Bromides; Chlorides; Fluorides; Iodides  
 —, detn., electrolytic, II, 700a  
 —, —, potentiometric, II, 706b  
**Haliotis rufescens**, II, *giganteus*, I, 1b, 201c  
**Halite**, VI, 173b  
**Hall process**, I, 268c  
**Halloysite**, III, 196a; VI, 174b  
**Halogen**, catalytic addition or substitution, II, 128c  
 —, detection in carbon compounds, II, 615b  
 —, detn. by hydrogenation, VI, 361b  
 —, —, Carius method, II, 620b  
 —, —, Grotte and Krekeler's method, II, 621c  
 —, —, micro-methods, II, 632a  
 —, —, Piria and Schiff's method, II, 621a  
 —, —, Stepanov's method, II, 621c  
 —, —, volumetric, II, 657c  
**Halogeno-acetic acids**, VI, 174c  
 —, aromatic compounds as antiseptics, IV, 30c  
**Halogens**, see also Bromine; Chlorine; Fluorine; Iodine  
 —, detn., gravimetric, in mixtures, II, 608a, 609a  
 —, —, volumetric, in mixtures, II, 659c  
 —, qualitative separation of Cl, Br and I, II, 565a  
**Halotrichite**, I, 289a; IV, 591d; VI, 176d  
**Haloxiline**, IV, 403b  
 "Halozone" disinfectant, IV, 20c  
**Halphen-Hicks test** for rosin, III, 295a  
 —, test for cottonseed oil, II, 167b; III, 411c  
**Halva**, I, 190a  
**Halvorsen process**, I, 268c  
**Hamamelin**, VI, 177a  
**Hamamelis and H. spp.**, V, 417a; VI, 89c, 177a  
**Hamamelitannin**, VI, 89c, 177b  
**Hamamelose**, II, 288d  
**Hambergite**, I, 685a; VI, 13c  
**Hamlinite**, V, 263c  
**Harden and Young ester**, V, 22d  
**Hardened fatty oils**, see also Hydrogenated fatty oils  
 —, —, food values, VI, 185d  
**Hardening oils**, methods, VI, 177d  
 "Hard lead," I, 445d  
 "Hard purple" china-stone, III, 32c  
**Hard surfacing** with oxy-acetylene, I, 116b  
**Hargreaves-Bird cell**, III, 53b  
**Hargreaves-Robinson process**, II, 428c  
**Harmala alkaloids** (see also Arkbine), VI, 186a  
**Harmaline**, VI, 186a  
**Harmalol**, VI, 186a

- Har an**, I. 406b; VI. 186a  
**Harmine**, VI. 186a  
**Harmotome**, I. 631b  
**Hartshorn oil**, II. 29c  
**Hashab**, I. 11d  
**Hashish**, II. 209c  
**Hatchettolite**, I. 685c  
**Hatschek's viscosity formula**, IV. 292d  
**Hausmannite**, VI. 189b  
**Hawkite**, IV. 556d  
**Hawk's eye**, III. 430a  
**Hawthorn**, H. perfume, VI. 189b  
**Hazelnut oil**, VI. 189d  
**Heather**, VI. 190a  
**Heat of activation**, II. 531d  
 — solution of salts, VI. 207c  
 — transfer processes, III. 321a  
**Heavy alloy**, VI. 190b  
 — hydrogen, *see* Deuterium.  
 — spar, I. 641b, 651a  
 — water, *see* Deuterium oxide.  
**Heberlein finishing**, V. 191a  
**Heckling of textiles**, II. 461c  
**Hedenbergite**, III. 573a  
**Hederin**, VI. 89c  
**Hedge-mustard seed oil**, VI. 190b  
**"Hedonal"**, VI. 190d  
**Hedyotine**, VI. 190d  
**"Hegonon"**, VI. 191a  
**Heide's**, C. von der, extractor, IV. 587d  
**Helenin**, II. 398d, 400c; VI. 191a  
**Helenin**, I. 175b  
**Helianthic acid**, VI. 191a  
**Helianthus spp.**, I. 497a; III. 406b  
**Helicin**, VI. 90a  
**"Helicon"**, I. 517d  
**Helicorubin**, VI. 168c  
**"Helindone"** colours, I. 232c  
**Heliodor**, I. 685b  
**"Helio"** dyes and pigments, IV. 230a, b  
**Heliotrope**, II. 25a, 517c  
 —, Alizarin, BB, I. 232b  
 —, Brilliant, 2R, I. 577a  
 —, perfume, VI. 191b  
 —, Tannin, I. 577a  
**Heliotropin**, VI. 191b  
**Helium**, III. 204c; VI. 191c  
 — -I and -II, VI. 197d  
 — and radioactivity, VI. 199a  
 —, balloon filling, VI. 190c  
 —, chemical properties, VI. 198d  
 —, critical constants, VI. 197c  
 —, detection and detn., VI. 199b  
 —, detn. (*see* Argon, detn.), II. 681d  
 — from springs, VI. 193a  
 — gas thermometer, VI. 199d  
 — in minerals, VI. 194b  
 — natural gas, VI. 193c  
 —, laboratory prepn., VI. 194d  
 —, liquefaction, VI. 197c  
 —, occurrence in cosmos, VI. 192c  
 —, — the earth's atmosphere, VI. 192d  
 —, — volcanic and hot-spring gases, VI. 192d  
 —, physical properties, VI. 196a  
 — production, VI. 195b  
 —, respiratory mixture, VI. 199c  
**Helium-II**, thermal. conductivity, VI. 198b  
 —, uses, VI. 199c  
**"Hella"** bush light, V. 480d  
**Hellandite**, VI. 199d  
**Hellebore**, *see also* Helleborus.  
 —, American, VI. 200d  
 —, green, VI. 200b  
 —, white, VI. 200c  
**Helleborein**, helleborin, II. 1c, 387b, c  
**Helleborus niger**, *H. viridis*, *H. spp.* (*see also* Hellebore), II. 1c, 387b; VI. 200b  
**Hellebrin**, II. 387b, c  
**Hellhoffite**, IV. 545d  
**Helmholtz double layer**, III. 284a  
**Helminthosporin**, V. 55a  
**Helminthosporium spp.**, pigments, V. 54d, 55d  
**"Helmitol"**, VI. 200d  
**Helvite**, III. 547a  
**Hematine Crystals**, IV. 126b  
**Hematite** (*see also* Hematite), VI. 160b  
**Hemellithenol**, VI. 201a  
**Hemicelluloses**, II. 59a, 463a; VI. 201a  
 — from straw and wood, VI. 201b  
**Hemihydrate** from gypsum, II. 130a  
**Hemimellitene**, hemimellitene, III. 457a  
**Hemimorphite**, II. 201b, 516; VI. 137a, 201d  
**Hempinic acid**, II. 230a; VI. 202c  
**m-Hempinic acid**, II. 09b; VI. 202c  
**isoHempinic acid**, VI. 202d  
**"Hemisina"** (*see also* Adrenaline), J. 147d  
**Hemlock (Conium)**, III. 324a  
 — alkaloids, III. 324c  
 —, lesser (*Althusa*), I. 160d  
 —, spruce resin, II. 201b; VI. 202d  
**"Hemostatine"**, I. 147d  
**Hemp**, I. 1a; II. 269c; V. 162c, 168b  
 —, Ambari, Deccan or Mesta, V. 164c  
 —, Canadian, III. 538b; VI. 422d  
 —, cottonisation, V. 162d  
 —, hurds, V. 162d  
 —, Manila (*see also* Abaca fibre), I. 1a; V. 164d  
 —, —, specification, V. 165b  
 —, Mauritius, V. 168a  
 —, Mesta, V. 164c  
 —, New Zealand, V. 165b  
 —, perennial Indian, I. 4c  
 —, resin, Indian, VI. 422c  
 —, Rozelle, III. 407b  
**Hemp, bowstring**, V. 168b  
**Hempseed oil**, IV. 80a; VI. 202c  
 — in paints, VI. 203c  
 —, Sunn, II. 461b; V. 163b  
**Henbane**, VI. 203c  
**Hendecenoic acid**, VI. 204c  
**Hendecolic acids**, VI. 204a  
**Heneguen fibre**, I. 165a; V. 166a  
**Henna**, VI. 171b, 204c  
 — reng, VI. 171b  
**Henry's law**, I. 6c; IV. 38b, 48b  
**Hentriacontane**, I. 200c; II. 119c, 262a  
**n-Hentriacontane** in cabbage, II. 182d  
**Heparin**, anticoagulant, II. 23c; VI. 205a  
**Hepar sicc.**, VI. 204d  
**Heptaethylene glycol**, IV. 379b  
**Heptaldehyde**, II. 422a; VI. 205a  
**n-Heptane**, I. 1d  
 —, luminescent oxidation, III. 23b  
**cycloHeptatriene**, III. 535b  
**n-Heptic acid**, VI. 205a  
**isoHeptic acid**, VI. 205b  
**Heptic acids**, VI. 205a  
**Heptylacetacetic acid**, ethyl ester, I. 64c  
**Heptyl alcohol**, VI. 205d  
**n-Heptylsuccinic acid**, VI. 205d  
**Herapathite**, III. 172c  
 — in cellophane, II. 443a  
**"Heralol"**, I. 75a  
**Herbacetin**, herbactrin, III. 407a  
**Hercynite**, IV. 279d  
**Herderite**, I. 685a  
**"Hermite fluid"** disinfectant, IV. 20d, 21b  
**"Heroin"**, I. 65d; VI. 205d  
**Herring oil**, V. 228d  
**"Hertolan"**, II. 264c  
**Herzenbergite**, VI. 206a  
**Herzynie**, VI. 237b  
**Hesperidin**, VI. 90a  
**Hesperitonic acid**, V. 61a  
**Hessite**, VI. 206a  
**Hessonite**, III. 183c; V. 429c  
**Hetero-auxin** (*see also* Growth factor), I. 558b  
**Heteroazeotropic mixtures**, IV. 51b  
**Heterogeneous reactions**, *see* Reactions, heterogeneous.  
 **$\beta$ -Heteroglucosidase**, II. 442c  
**Heteroxanthine**, and synthesis, VI. 206b  
**Heteroazeotropy**, IV. 51c  
**"Hetocresol"**, VI. 224d  
**Hevea brasiliensis**, I. 20b; IV. 86c; VI. 91a  
**Hewettite**, VI. 224d  
**Hexaborane**, II. 40d  
**Hexacyanogen**, VI. 224d  
**n-Hexadecane dicarboxylic acid**, VI. 225d  
 **$\Delta^6$ -Hexadiene**, II. 156d; III. 573a  
**cycloHexadiene**, III. 535b  
**Hexahydrate**, IV. 321b  
**Hexahydrobenzene**, VI. 225c  
**Hexahydrocarbazole**, II. 279a  
**Hexahydrofarnesol**, IV. 591b  
**Hexahydrophenol**, VI. 225d  
**Hexaldehyde**, VI. 225b  
**"Hexalin"**, I. 147d; VI. 225d, 354a  
**"Hexamecoll"**, VI. 225b  
**Hexamethylcarbamylamine** ferro-salts, III. 475b  
**Hexamethylene**, VI. 225c  
**Hexamethylenetetramine**, I. 195a; V. 320b  
 — antiseptic, IV. 27d  
 — borate, II. 53b  
 — camphorate, I. 357d  
 — compound with bromal, II. 106b



- Hexamethylenetetramine**,  
detection, V. 298b  
— in casein paints, II. 415b  
—, respirators, III. 18b  
—, phosgene absorbent, II. 322a  
—, preservative, V. 297d  
—, trade names, I. 326a  
**Hexamethylenetetraminetri-  
guaiacol**, VI. 141c  
**Hexamethylenetriperoxide-  
diamines**, IV. 513b  
"Hexamine," I. 326a  
—, antiseptic, IV. 27d  
**cycloHexane**, VI. 225c  
**cycloHexanol**, II. 308d; VI.  
225d  
—, dehydrogenation, II. 427d  
**cycloHexanols**, prepn., II.  
426d; VI. 353d  
"Hexanon," I. 380d  
**cycloHexanone** in lacquers, II.  
472a  
**cycloHexanones**, prepn., II.  
426d; VI. 353d  
**cycloHexanone**, trade names,  
I. 380d  
**Hexatriene**, II. 151a  
**cycloHexene**, I. 467b; III.  
533a  
**Hexitols**, VI. 494a  
"Hexogen," III. 535d  
**Hexoic acids**, II. 271b  
**Hexokinase**, V. 24c, 35c; VI.  
77d  
"Hexophan," VI. 226b  
**Hexose**, breakdown by yeast,  
II. 99b  
**Hexosediphosphate**, fermenta-  
tion in presence of  
adenylic acid, V. 39a  
—, — — — arsenite, V.  
39b  
— in fermentation and in  
muscle extract, see Fer-  
mentation, alcoholic; Gly-  
colysis.  
**Hexose phosphate**, II. 295d  
**Hexosephosphoric esters**, V.  
21b  
**Hexuronic acid**, I. 502a  
**cycloHexyl acetate** in lacquers,  
II. 472a  
**n-Hexyl alcohol**, VI. 226b  
**Hexyl butyrate**, occurrence, II.  
179c  
**Hexylformal**, I. 34b  
**cycloHexylformal**, I. 34b  
**cycloHexylcyclohexene**, III.  
533c  
**Hexyl iodide** from glucoses, II.  
285b  
"Hexyl" or Aurantia, I. 549c;  
IV. 14d, 480a  
**Hexylresorcinol**, II. 271d  
**Hibbenite**, VI. 265d  
**Hibiscus spp.**, III. 407b; V.  
164c; VI. 90b  
**Hiddenite**, VI. 226b  
"Hiduminium," I. 253b, 277a  
**Hieratite**, V. 60b  
**Highgate resin**, III. 340d  
**High temperature carbonisa-  
tion**, V. 367b, 450, 451  
**Hiriogane**, VI. 230b  
**Hilgardite**, VI. 230c  
**Hink's test** for coconut fat, II.  
167a  
**Hippocastanin**, III. 27b; VI.  
278d  
**Hippulin**, VI. 269a, c  
**Hiptagin**, VI. 80a  
**Hirsutidin**, III. 554c; VI.  
230c  
**Hirsutin**, III. 554c; VI. 231a  
**Hirudin**, II. 24c  
**Hispidogenin**, II. 385d  
**Histamine**, IV. 331d  
**Histidine**, VI. 231c  
**d-Histidine**, VI. 234c  
**dl-Histidine**, VI. 234b  
**Histidine and B. coli**, VI. 235c  
— and ultra violet therapy, VI.  
235b  
—, derivs., VI. 237b  
—, detection and detn., VI.  
233c  
— from carnosine, II. 392c  
— in cabbage, II. 182d  
—, photochemistry, VI. 234d  
—, prepn., VI. 232b  
— salts, VI. 236b  
— synthesis, VI. 233b  
**l-Histidine**, properties, VI.  
234d  
**Histine**, VI. 233a  
**Histones**, VI. 231d  
**Histozyme**, IV. 315a  
**Hittorf transport number**, VI.  
237d, 296b  
**Hiviscin**, VI. 90b  
**H.M.T.D.**, IV. 513b  
**Hochofen cement**, II. 145b  
**Hofmann degradation**, II. 375a  
**Hofmeister** or lyotropic series,  
III. 280d  
**Hofsäss burner**, V. 217a  
**Holarrhena spp.**, alkaloids, III.  
321d, 322c, 323d  
**Holarrhenine**, III. 322c, 323a, d  
**Holarrhmine**, III. 322b, 323a, d  
**Holarrhine**, III. 322c, 323a, d  
**Hollandite**, VI. 239b  
**Hollands**, V. 532b  
**Hollyhock**, I. 264a  
**Holmes still**, I. 346c  
**Holmia**, II. 511d; VI. 240b  
**Holmium**, II. 511c; VI. 239d  
— chloride, VI. 240b  
— sesquioxide, VI. 240b  
— sulphate octahydrate, VI.  
240b  
"Holocaine," I. 304d, 369c; VI.  
240b  
"Holoklastit," IV. 404a  
"Homatropine," VI. 240c  
**Homborg's phosphorus**, II.  
213b  
**β-Homobetaine** from carni-  
tine, II. 391c  
**Homocamphenilone**, II. 238b  
**Homocamphoric acid**, II. 211c  
**Homocaronic acid**, II. 389b  
**Homocaryophyllenic acid**, II.  
409b  
**Homocatechol**, VI. 240c  
**Homocelidonine**, II. 527d  
"Homocol," III. 515b  
**Homoeiodictyol**, IV. 333d  
**Homoeuonysterol**, IV. 400c  
**Homogenisers**, IV. 205c  
**Homogenitisic acid**, VI. 261c  
— — lactone, VI. 262a  
**Homophleine**, IV. 336a  
**Homophilic acid**, VI. 262c  
**Homopyrocatechol**, VI. 240c  
**Homocoumarin**, III. 160d  
**Homocoumaron**, I. 147d  
**Homoterpenylic acid** from  
carene, II. 389d  
**Homovanillin**, IV. 396a  
**Homoseotropic mixtures**, IV.  
51b  
**Homra cement**, II. 145d  
**Honewort**, VI. 262c  
**Honey**, VI. 262d  
—, ash, VI. 264c  
—, buckwheat, conifer, and  
honey-dew, VI. 263c, d  
—, detection of adulteration,  
VI. 264d  
"Honey," Ethiopian mosquito,  
VI. 263b  
**Honey**, Eucalyptus, VI. 263b  
"Honey," palm, VI. 263b  
**Honey**, preservation with  
sodium benzoate, VI. 264b  
**Honeysuckle perfume**, natural  
and artificial, VI. 265c  
**Honey**, "virgin," VI. 264a  
—, vitamin content, VI. 264d  
"Honthin," VI. 265d  
"Hoolamite" in respirators,  
III. 21a  
"Hopcalite," II. 347a, 351c,  
682c; III. 10b, 20d  
**Hopea spp.**, III. 546b  
**Hopite**, VI. 265d  
**Hopkinson pressure bar test**,  
IV. 549a  
**Hop oil**, caryophyllene in, II.  
408d  
**Hops**, II. 91c  
— as preservatives, V. 297b  
**Hordein**, I. 647d  
— in mulling, II. 88d  
**Hordeinine**, VI. 266a  
— salts, VI. 266b  
**Hordeum spp.**, I. 645b  
**Hormone**, antidiabetic, VI.  
406d  
—, corpus luteum, VI. 272c  
—, pancreatic, VI. 268c  
—, parathyroid, VI. 268b  
—, pitocin, VI. 267b  
—, pitressin, VI. 267a  
**Hormones**, V. 63b; VI. 266c  
—, adrenal, VI. 270c  
—, androgenic, VI. 274b  
—, —, biological assay, VI. 274b  
—, gonadotropic, VI. 266d  
—, melanophoric, VI. 267b  
—, oestrogenic, VI. 268c  
—, oxytocic, VI. 267a  
—, pituitary gland, VI. 266d  
—, plant, VI. 138b  
—, pressor, VI. 267a  
**Hormone**, thyroid, VI. 267b  
—, vasopressin, VI. 267a  
—, wound, VI. 158d  
**Hornblende**, II. 137c; VI.  
279a  
— asbestos, I. 490c  
— basalt, I. 652a  
**Hornfels**, see Hornstone.  
**Horn-quicksilver**, VI. 279a  
**Hornsilver**, II. 481b; VI. 279b  
**Hornstone**, I. 46; VI. 279b  
**Horse-bone fat**, VI. 280d  
— chestnut, VI. 279b  
— —, saponin, VI. 279d  
— chestnuts, acetone and butyl  
fermentation, VI. 279d  
— —, butyl alcohol from, VI.  
279d  
— fat, VI. 280a  
— flesh-ore, II. 32d  
— meat, identification test,  
VI. 280b  
"Horse-oil," VI. 280a  
**Horse-radish**, VI. 280d

- Horses'** crest-fat, VI. 280c  
**Horse's** foot oil, VI. 280d  
**Howlite**, I. 586a  
**Huantajayite**, VI. 173d  
**Huckleberry**, VI. 281b  
**Huile surtine de Gambin**, I. 455c  
**Huleite**, VI. 281b  
**Hume-Rothery's** rule, VI. 281c, 282b  
**Humic** acid, VI. 284c  
**Humidification**, VI. 280c  
**Humidity** and humidity control, VI. 284d  
 — control, automatic, VI. 287b  
 —, detn. of water vapour, II. 685d  
 —, experimental, VI. 287c  
 —, detn., VI. 285b, 286a  
 —, industrial importance, VI. 287d  
 —, relative, VI. 285a  
**Humulene**, humulon, II. 92a, 408d  
 —, nitroso-, II. 100a  
**Hutchinsonite**, VI. 288c  
 — "**Hver-salt**," VI. 176d  
**Hyacinth**, VI. 288d  
 — perfume, artificial, VI. 288d  
**Hyacinthin**, artificial, II. 118d  
**Hyanic** acid, VI. 289a  
**Hyalophane**, I. 631b  
**Hydantoin**, VI. 289a  
 — 5-acetic acid, VI. 203b  
 —, 5-amino-, hydrochloride, VI. 290a  
 —, condensation with aldehydes, VI. 290c  
 — 1,3-diacyetyl-, VI. 290b  
 — 1,3-dichloro-, VI. 290b  
 — homologues, VI. 291d  
 — 5-nitro-, VI. 290a  
 — physiological action, VI. 289c  
**Hydantoins**, I. 320b  
**Hydrocarpic** acid, II. 521b  
 — in chaulmoogra oil, II. 521b  
**Hydnocarpus** oil, II. 521d  
**Hydracetyl-acetone**, I. 30c  
 — "**Hydraldite**," V. 320c  
 — "**Hydramin**," VI. 294b  
**Hydrargillite**, I. 261c, 284b;  
 V. 532a  
 — "**Hydrargyrol**," VI. 294b  
**Hydrastine**, VI. 294b  
**Hydrastine**, VI. 295b  
**Hydrastis** alkaloids, II. 261b  
**Hydrastis canadensis**, I. 620b, 082d; VI. 294b  
**Hydration**, catalytic, II. 428a  
**Hydrato-kanten- $\delta$**  and  $-\gamma$ , I. 163a  
**Hydratopektin**, V. 162a  
**Hydraulic** main in gas manufacture, V. 447d  
**Hydrazides**, luminescent oxidation, III. 23d  
 —, preparation, II. 371c  
**Hydrazine**, VI. 298d  
 —, compounds with chromium, III. 109d  
 —, detection, II. 572b; V. 299b  
 —, detn., volumetric, II. 603d  
 —, 2,4- and 3,5-dinitrobenzoyl-, I. 197a  
 —, qualitative reactions, II. 572b  
**Hydrazines**, VI. 298c  
**Hydrazobenzene**, VI. 301d  
**Hydrazoic** acid (*see also* Azonimides), prepn. and derivs., I. 580a  
 —, qualitative reactions, II. 572b  
**Hydrazones**, VI. 302a, 304c  
 —, relation to azo compounds, VI. 302c  
 — of sugars, II. 292b  
 —, oxidation, VI. 304a  
**Hydrazotoluenes**, VI. 304d  
**Hydrides**, VI. 305a  
 —, interstitial, VI. 305b  
 —, salt-like, VI. 305a  
 —, unclassified, VI. 305c  
 —, volatile, VI. 305a  
**Hydrindone**,  $\alpha$ - and  $\beta$ -, VI. 305c, 306b  
**Hydroabietic** acid, I. 3a  
**Hydroacridines**, I. 128b  
**Hydrobenzamide**, I. 195a;  
 VI. 99a  
**Hydrobromic** acid, II. 117a, 428d  
**Hydrocarbons**, aromatic, in petroleum, I. 466c  
 —, dehydrogenation, to lamp-black, II. 313a  
 — in candelilla wax, II. 262a  
 —, photographic dopes, II. 418b  
 —, paraffin, detn., II. 684b  
 —, reaction with phenyl isocyanate, II. 361a  
 —, synthesis from water gas, II. 350b, 425c  
 —, unsaturated, detn. by gas analysis, II. 677c  
**Hydrocellulose**, chain length, II. 302a  
 —, in photography, II. 447c  
**Hydrocerussite**, VI. 308b  
**Hydrochloric** acid, II. 428d;  
 III. 69a  
 — "**Hydrochloric** acid number," VI. 161a  
**Hydrochloric** acid, solvent in analysis, II. 549b  
 — ether, IV. 358b  
**Hydrocinchene**, III. 161b  
**Hydrocinchonine**, III. 163c  
**Hydrocinchonidine**, III. 128a, 153b, 162b  
 —, hydroxy-, III. 153c  
 —, iodo-, III. 153b  
**Hydrocinchonine**, III. 128a, 148a, 162d, 164a  
 —, bromo-, III. 156a  
 —,  $\alpha$ -hydroxy-, III. 157a  
 —, iodo-, III. 156a  
**Hydrocinchoninone**, III. 163d  
**Hydrocinchotoxine**, III. 163c  
 —, N-benzoyl-, oxidation, III. 146a  
**Hydrocinnamic** acid, III. 181b  
**Hydrocinnamoin**, III. 180c  
**Hydrocupreicene**, III. 168a  
**Hydrocupreidine**, III. 137d, 185c  
 — formation, III. 149a  
**Hydrocupreine**, III. 137a, 161b, 167c  
 — formation, III. 149a  
**Hydrocupreinotoxine**, III. 168a  
**Hydrocyanic** acid (*see also* Cyanides), III. 492c, 500a, 501d  
 —, detection and detn. of gaseous, II. 683c; III. 501a  
**Hydrocyanic** acid from amygdalin, I. 357d; IV. 282c  
 — — plant glycosides (*see also* Amygdalin), II. 237a, 418c, 483d; III. 409b, 531b; VI. 83d  
 — in fumigation, III. 502b;  
 V. 392d  
 — — warfare, III. 10b  
 —, physical properties, III. 501a  
 — from ammonia and acetylene, III. 490c  
 — carbon monoxide, III.  
 — ethylene, III. 496d  
 — hydrocarbons, III. 496b  
 — methane, III. 497a  
 — ferrocyanides, III. 492c  
 — formamide, III. 495a  
 — nitrogen and hydrocarbons, III. 498b  
 — schlempe, III. 493a  
 — thiocyanates, III. 492d  
 — toxic action and antidotes, III. 500c  
**Hydroergotinine**, *see* Ergotoxime  
**Hydroeugenol**, ammechloro-, IV. 396c  
**Hydroferrocyanic** acid (*see also* Ferrocyanides), III. 471b  
**Hydrofluoric** acid, *see also* Fluorides; Fluorine; Hydrogen fluoride  
 —, aqueous, V. 280c  
 —, solvent in analysis, II. 519d  
**Hydrofluosilicic** acid, V. 282b  
**Hydrogen**, VI. 308c  
 — absorbs in gas analysis, VI. 358a  
 —, active, VI. 320a  
 —, adsorption, VI. 311c  
 — and metallic oxides, VI. 319d, 331c  
 — asmele, I. 472d  
**Hydrogenated** fats, nickel m., VI. 185c  
 — fatty oils (*see also* Hardened fatty oils), VI. 177b  
 —, reduction of unsaturated esters, VI. 177b  
 —, Schmidt's process, VI. 177c  
 — oils, properties, VI. 183c  
 —, test for, VI. 185b  
**Hydrogenation**, VI. 347c  
 —, "Adams' catalyst," VI. 348c  
 — analysis, destructive, VI. 359b  
 — as dehalogenation process, VI. 359a  
 —, Bedford and Williams' process, VI. 178c, 179a  
 —, Birkeland and Devik's process, VI. 179c  
 —, Bolton and Lush's process, VI. 182b, 183b, 185b  
 —, Bolton's process, VI. 180a  
 —, Calvert's process, VI. 179b  
 — catalysts, poisons, VI. 350b  
 —, prepn., VI. 180b  
 —, Lane's process, VI. 180b

**Hydrogenation**, catalytic, VI. 177*d*  
 —, —, of hydrocarbon oils, VI. 178*b*  
 —, —, theories of, VI. 372*c*  
 —, colloidal platinum and palladium catalysts, VI. 349*b*  
 —, continuous processes, VI. 182*a*  
 —, "copper chromite" catalysts, VI. 419*d*  
 —, Dewar and Liebmann's apparatus, VI. 179*a*  
 —, Ellis' method, VI. 179*a*  
 —, Erdmann's processes, VI. 178*c*  
 —, experimental conditions, VI. 350*a*  
 —, Lane's apparatus, VI. 179*b*  
 —, liquid-phase apparatus, VI. 348*a*  
 —, Maxted and Ridsdale's apparatus, VI. 179*d*  
 —, McKelroy's process, VI. 179*c*  
 —, mechanism, VI. 372*c*  
 —, Mellersh-Jackson's apparatus, VI. 179*d*  
 —, micro-methods, VI. 318*b*  
 —, Moore's method of subdivision, VI. 179*b*  
 —, nickel catalysts, VI. 349*b*  
 —, Normann's process, VI. 178*a*  
 —, of acetylenic compounds, VI. 352*a*  
 —, —, amides, VI. 358*b*  
 —, —, aromatic acids and amines, VI. 354*b*  
 —, —, nuclei, VI. 352*a*  
 —, —, azo-compounds, VI. 358*c*  
 —, —, benzene derivs., VI. 353*d*  
 —, —, carbonyl compounds, VI. 355*c*  
 —, —, coal tars, VI. 371*c*  
 —, —, cotton-seed oil, VI. 184*a*  
 —, —, double and triple bonds, VI. 370*b*  
 —, —, ethylenic compounds, VI. 351*c*  
 —, —, fatty oils, VI. 177*b*  
 —, —, furfural, VI. 355*b*  
 —, —, heterocyclic compounds, VI. 351*d*  
 —, —, oleic acid, electrolytic methods, VI. 177*c*  
 —, —, vapour, VI. 178*a*  
 —, —, phenol, VI. 353*d*  
 —, —, pyridine, VI. 351*d*  
 —, —, quinaline, VI. 351*d*  
 —, —, palladium catalysts, VI. 349*a*  
 —, —, platinum catalysts, VI. 348*c*  
 —, —, pressure, VI. 348*b*  
 —, —, processes, VI. 177*d*  
 —, —, Raney nickel catalyst, VI. 349*b*  
 —, —, Ruben's apparatus, VI. 180*a*  
 —, —, Sabatier and Senderens' process, VI. 177*d*  
 —, —, Schwoerer's apparatus, VI. 178*b*  
 —, —, selective, VI. 350*c*, 351*a*, 356*c*  
 —, —, solvents in, VI. 350*a*  
 —, —, Testrup's process, VI. 178*d*  
 —, —, "T.R.W. interchange process," VI. 182*c*  
 —, —, vapour-phase, VI. 178*a*, 347*c*  
 —, —, Walker's process, VI. 179*b*  
 —, —, Wilbuschewitsch's process, VI. 178*d*

**Hydrogen**, bacterial production, V. 44*a*  
 —, bromide, *see* Hydrobromic acid.  
 —, catalytic production, II. 425*a*  
 —, chloride, *see* Hydrochloric acid.  
 —, cyanide, *see* Cyanides; Hydrocyanic acid.  
 —, detection, II. 683*b*  
 —, detn., II. 678*d*, 683*b*; VI. 312*c*  
 —, electrode, VI. 335*c*  
 —, fluoride (*see also* Hydrofluoric acid), V. 278*d*  
 —, liquid, as catalyst, VI. 260*b*  
 —, for balloons, VI. 331*a*  
 —, —, catalytic processes, VI. 182*c*  
 —, from acids, VI. 310*b*  
 —, —, alkalis, VI. 310*c*  
 —, —, cracked ammonia, VI. 335*a*  
 —, —, ethyl alcohol, Haag process, VI. 332*d*  
 —, —, hydrides, VI. 305*b*, 311*c*, 330*b*  
 —, —, hydrocarbons and organic compounds, VI. 311*d*  
 —, —, methane, II. 319*c*  
 —, —, reduction of steam, VI. 310*d*, 325*c*  
 —, interchange reactions with deuterium, III. 563*c*  
 —, ion, VI. 295*d*, 297*c*  
 —, —, catalysis by, VI. 253*c*  
 —, —, concentration, catalytic measurement, VI. 251*b*  
 —, —, stability test for explosives, IV. 534*d*  
 —, —, detn., VI. 335*a*  
 —, —, "acid error," VI. 337*d*  
 —, —, antimony electrode, VI. 339*b*  
 —, —, "Buffer solutions," VI. 337*c*  
 —, —, colorimetric "comparators," VI. 337*b*  
 —, —, methods, VI. 337*a*  
 —, —, glass electrode, VI. 338*c*  
 —, —, "protein error," VI. 337*d*  
 —, —, quinuhydrone electrode, VI. 338*a*  
 —, —, "salt error," VI. 337*d*  
 —, —, its nature, VI. 247*b*  
 —, —, litre-weight, VI. 313*a*  
 —, —, manufacture, VI. 371*a*  
**Hydrogenolysis** of aromatic oxygen in  $\alpha$ -position, VI. 350*c*  
**Hydrogen**, ortho-para conversion, VI. 373*d*  
 —, overpotential, III. 376*b*  
 —, peroxide, VI. 339*b*  
 —, —, as bleaching agent, VI. 340*c*  
 —, —, disinfectant and preservative, IV. 19*a*; V. 304*a*; VI. 346*d*  
 —, —, "autoxidation" reactions, VI. 340*c*  
 —, —, catalysts, poisons for, VI. 340*a*  
 —, —, catalytic decomposition at surfaces, VI. 346*a*

**Hydrogen peroxide**, catalytic decomposition by catalase, II. 422*c*  
 —, —, colloidal Pt, II. 530*b*  
 —, —, haemin, VI. 349*a*  
 —, —, iodide ions, VI. 258*b*  
 —, —, detection, II. 574*a*; VI. 340*d*  
 —, —, detn., II. 604*d*; V. 301*c*; VI. 340*d*  
 —, —, potentiometric method, II. 707*c*  
 —, —, formation and prepn., VI. 340*a*, 341*b*  
 —, —, from anthraquinone, VI. 340*d*  
 —, —, in biological material, VI. 339*d*  
 —, —, cotton bleaching, II. 10*d*  
 —, —, food, detection and detn., V. 301*c*  
 —, —, luminescent decomposition, III. 23*c*  
 —, —, prepn., barium peroxide process, VI. 342*d*  
 —, —, persulphate process, VI. 341*b*  
 —, —, properties, VI. 343*b*  
 —, —, reaction with formaldehyde, VI. 345*a*  
 —, —, thiosulphates, VI. 258*c*  
 —, —, persulphide, II. 230*d*  
**Hydrogen**, physical properties, III. 563*a*; VI. 312*c*  
 —, production and purification, I. 334*c*  
 —, —, by electrolysis, I. 335*a*; VI. 309*b*, 323*b*  
 —, —, fermentation, V. 44*a*  
 —, —, Fernbach - Weizmann's process, II. 169*c*; VI. 332*d*  
 —, —, ionic displacement, VI. 309*d*  
 —, —, partial liquefaction, I. 335*a*; VI. 331*c*  
 —, —, closed electrolytic cells for, Electrolys or Levin, National Electrolyser, Roth (I.G.), Schmidt-Oerlikon, Siemens, VI. 324*b*  
 —, —, costs of commercial, VI. 332*d*  
 —, —, cracking of hydrocarbons, VI. 331*b*  
 —, —, electrolytic cells for, Bamag Zdzansky, Fauser, Holmboe, Knowles, Schoop, VI. 323*c*  
 —, —, from coke-oven gas, I. 335*a*  
 —, —, water gas (*see also* Ammonia synthesis; Catalysis in industrial chemistry; Gas, water), I. 334*c*; II. 349*a*; VI. 325*c*, 371*a*  
 —, —, Hydrolith process, VI. 311*c*, 330*b*; VI. 381*a*  
 —, —, iron - steam processes, Bamag, Lane, Messerschmitt, VI. 328*b*  
 —, —, Liljenrot process, VI. 311*c*, 330*a*  
 —, —, methane-steam reaction, II. 425*b*; VI. 330*d*

- Hydrogen production, pressure electrolyzers for**, Niederreither, Noeggerath, VI. 324d
- , purification of water gas, I. 384d, 424d; VI. 326a
- , Silicol process, VI. 330d
- , water gas generators (*see also* Gas, water), Bubiag Didier, Lurgi, Pintsch-Hillebrand, Viag, Winkler, VI. 327b, 328a
- , pure, prepn., VI. 312a
- , reactions, VI. 315d
- , reaction with carbon, VI. 318a
- , —, — dioxide, VI. 318b
- , —, — monoxide, II. 349c, 425c; VI. 318b, 333d
- , —, —, alcohols from, II. 425c; VI. 334a
- , —, —, chlorine, VI. 310b
- , —, —, halogens, VI. 316a
- , —, —, hydrocarbons, VI. 310a
- , —, —, metals (*see also* Hydrides), VI. 319b, c, 334d
- , —, —, nitrogen, I. 332a; II. 423d; VI. 317d
- , —, —, oxygen (*see also* Explosions, gaseous), VI. 316d
- , spectra, VI. 321c
- , sulphide, carbon disulphide from, II. 337c
- , —, detection, II. 574b, 683d
- , —, detn., II. 666c, 683d
- , —, in carbon disulphide, II. 338c
- , —, —, warfare, III. 10c
- , —, oxidation, II. 424d
- , —, reaction with carbon suboxide, II. 352d
- , —, —, carvone, II. 400d
- , —, removal from town gas, II. 319d; V. 401c
- "Hydrogen swells,"** V. 291a
- Hydrogen welding, atomic**, VI. 334b
- Hydroipecamine**, IV. 281a
- "Hydrolyses,"** VI. 248c
- Hydrolysis**, VI. 381a, 386a
- , by enzymes (*see also* Amylase; Enzymes; Fermentation; Glycosides), VI. 395a
- "Hydrolysis constant,"** VI. 248c
- Hydrolysis**, effects in titrations, II. 638b
- "Hydrolysis"** of ammonium acetate, VI. 248b
- , —, chloride, VI. 247b
- Hydrolysis of esters**, VI. 241d, 257c
- , a —, acid and alkaline, VI. 385d, 388c
- , —, ethyl acetate, catalytic, VI. 244a
- , —, glycosides, VI. 394a
- , —, organic halides, VI. 383c
- , —, salts, VI. 381b
- , —, sugars, II. 530d; VI. 384a, c
- Hydromagnesite**, VI. 398d
- Hydrometer**, Beck's, I. 188c
- , Clarke's, I. 185b
- , Sikes', I. 187d
- Hydronalium**, I. 253b, 277c
- Hydrophilic colloids**, III. 279d
- Hydrophobic colloids**, III. 279d
- I. 453b
- , III. 187c
- Hydroquinidine**, III. 166c
- Hydroquinidine**, III. 128a, 145b, 164d
- , chloro-, III. 170c
- , iodo-, III. 170c
- Hydroquinine**, III. 128a, 135a, 166a
- , chloro-, III. 175a
- , iodo-, III. 175b
- , synthesis, III. 144a
- Hydroquinone**, III. 167a
- Hydroquinone and its ethers**, VI. 399a, c
- , detn., potentiometric, II. 707c
- , dimethyl ether, IV. 6d
- Hydroquinotoxine**, III. 166c
- , synthesis, III. 145a
- "Hydrosulphite conc. special,"** I. 575d
- Hydrosulphite**, detn., volumetric, II. 666a
- Hydrosulphites**, *see also* Hyposulphites.
- Hydroxamic acids**, prepn., II. 371c
- Hydroxonic acid**, VI. 290a
- Hydroxonium ion**, VI. 247c
- "Hydrox powder,"** IV. 562c
- Hydroxy-acids** (*see also* Carboxylic acids; Hydroxybutyric acids; Hydroxystearic acids), VI. 400a
- , —, alcoholic and phenolic, VI. 400a, 401a
- Hydroxylamine**, VI. 402a
- , detection and detn., VI. 403b
- , detn., volumetric, II. 663d
- , nitro-, oxidising agent, II. 362b
- , nitroso- $\beta$ -, III. 335b
- , qualitative reactions, II. 572b
- , sulphonic acids, VI. 402d
- Hydroxyl group**, detn., II. 624c
- , ion, catalysis by, VI. 253c
- , concentration, catalytic measurement, VI. 251b
- , —, nature, VI. 248a
- Hydrozincite**, VI. 406a
- Hydurilic acid**, VI. 406a
- Hygric acid**, III. 226a
- Hygrine**, III. 225d
- Hygrometers**, wet and dry bulb, VI. 285b
- Hyodeoxycholic acid**, I. 689b
- Hyoscine**, VI. 203d
- Hyoscyamine**, VI. 203d
- Hyoscyamus niger**, VI. 203c
- Hyaconitine**, I. 122b
- Hypaphorine**, I. 686d; VI. 464c
- Hypericin**, V. 55d
- "Hyperol,"** VI. 345d
- Hypersthenes**, IV. 311a; VI. 408a
- "Hypnal,"** VI. 408b
- "Hypnogen,"** VI. 408b
- "Hypnone,"** I. 71a; VI. 408b
- Hypo** (*see also* Thiosulphates), I. 433b
- Hypobromous acid**, II. 117c
- Hypochlorite**, detn., potentiometric, II. 707c
- , —, volumetric, II. 609d, 657b
- , in cotton bleaching, II. 6a
- Hypochlorites**, qualitative reactions, II. 576c
- Hypochlorous acid**, addition to olefins, II. 152a
- Hypophasic pigments**, II. 898d
- Hypophosphites**, qualitative reactions, II. 573a
- Hypophosphorous acid**, detn., II. 665c
- Hypophysis**, VI. 266d
- Hyposulphite**, detn., gravimetric, II. 609b
- Hyposulphites** (hydrosulphites) qualitative reactions, II. 574b
- Hyposulphurous** (dithionous) acid, detn., volumetric, II. 660d
- Hypoxanthine**, II. 108a; VI. 408b
- , detn., VI. 409d
- , occurrence, II. 197a, 390d
- , synthesis, VI. 408d
- Hypoxonitine**, I. 122d
- "Hyalrite,"** V. 320c
- "Hyrgol,"** VI. 409d
- Hystazarin**, I. 212d, 222c, 402c
- , 1,4-dinitro-, I. 362c
- , methyl ether in hay root, II. 524c
- , 1-nitro-, I. 392c
- "Hysterol,"** VI. 159c
- Hyzone**, VI. 321d, 322d
- I
- Ianthinite**, I. 661b; V. 410a
- Ianthone**, VI. 410a
- Ibogaine**, VI. 410b
- Icaco**, VI. 410c
- Ice colours** (azoic dyes), IV. 133c, 193a, 227b
- Iceland moss**, VI. 410c
- , spar, II. 203c
- , fusion, II. 220b
- Ice-spar**, III. 440b
- Ichthammol**, VI. 410c
- "Ichthol,"** VI. 410c
- Iconogen** ("eikonogen") test for potassium, II. 553d
- Icosane**, VI. 410c
- "Icyl"** colours, IV. 234a
- Idasin**, VI. 411a
- , relation to cyanidin, III. 116a
- Ideal gas**, and definition, VI. 412a, 413d
- Ideose**, II. 285d
- d-Iditol**, II. 296d
- Idocrase**, IV. 279d; VI. 414a
- Idryl**, V. 269c
- "Iglodine,"** VI. 414b
- "Igmerald,"** IV. 279b; V. 513a
- Ignition**, *see also* Inflammability; Inflammable mixture.
- , by electric sparks, IV. 426c
- , limits and pressures, IV. 417d, 422d, 427d; V. 237a
- , phenomena, IV. 417b
- , point diagram, IV. 426a
- , temperatures, detn., IV. 419d, 421d
- , influence of time-lag, IV. 420a
- , of combustibles, IV. 425d
- , —, gases, IV. 420b; V. 237d
- , —, liquid fuels, IV. 421b

**Ignotine**, II. 392a

**Ilax vomitoria**, VI. 414b

**Ilcyl alcohol**, I. 692d

**Ililium**, II. 511c; VI. 414b

**Ilipé butter**, I. 643a, 653c; II. 168d

**Ilipene**, I. 653d

**Ilipé nuts**, II. 31d, 32a

**Ilipé spp.**, I. 653a, c, 654a, 655b

**Ilipé tallow** in cacao butter, II. 187c

— in chocolate, III. 88b

**Iluric acid**, III. 338b

**Ilmenite**, I. 650d; II. 303b; VI. 414d

**Ilvaite**, VI. 415b

**Ilmides**, II. 371a, 375c

**$\beta$ -Iminazoly- $\alpha$ -aminopropionic acid**, VI. 231c

**Imines**, VI. 415b

**Iminochlorides**, reduction, II. 374b

**Imino-groups**, defn., II. 627d

"**Imogen**," VI. 415d

— sulphate, VI. 415d

**Imperialine**, V. 330a

**Improvers** in flour, II. 81b

**Incarnatrin**, III. 207a; VI. 90b

**Indaconine**, I. 123a

**Indaquinine**, I. 122d

**Indamines**, I. 573a; VI. 416c

**Indanones**, VI. 305d

**Indanthrene**, I. 100c, 111d, 414c

— colours, I. 414-427

**Indanthrones**, I. 205a, 206a, 411d, 414d

**Indazine**, I. 577c

**Indene and derivs.**, VI. 419a, 421d

**Inderite**, VI. 422c

**Indian berry**, I. 370a; III. 220c

— buffalo grass, II. 182d

"**Indian butter tree**," I. 651a

**Indian fire**, I. 663b

— liquorice, I. 4c

**Indican**, VI. 90b, 434c, 436b

—, detection, VI. 436d

**Indicanin**, VI. 436b

**Indican**, synthesis, VI. 437a

—, urinary, VI. 465c

**Indicator exponent**, VI. 426c

**Indicators**, II. 637d; VI. 337d, 425d

—, adsorption, II. 650a, 658a; VI. 431a

—, external, VI. 425d

—, fluorescent, VI. 429b

—, in volumetric analysis, II. 637d

—, neutralisation, VI. 426a

—, oxidation-reduction, VI. 429c

—, radioactive, VI. 432a

—, surface colour changes, VI. 428c

**Indifulvin**,  $\alpha$ - and  $\beta$ -, VI. 436b

**Indifuscin**, VI. 436b

**Indigo**, IV. 120c

—, Alizarin, G. I. 233a

—, analysis, VI. 439c

—, Carmine, IV. 129c; VI. 450a

—, copper (covellite), III. 341c, 355b, 413d

—, cultivation, VI. 433c

—, 4:5-, and 4':5'-diphthaloyl-, I. 412b

—, enzyme, VI. 437c

**VOL. VI.**—37

**Indigo extract**, IV. 129c; VI. 450a

—, extraction, VI. 436a

**Indigofera spp.**, VI. 90b; VI. 433c

**Indigo-gluten**, VI. 434d, 439a

**Indigoid dyes**, VI. 451b

—, identification, IV. 151d, 156a; VI. 456d

**Indigo**, leuco-, *see* Indigo White.

—, manufacture, VI. 431b

—, natural, VI. 432c, 433a

—, root, wild, I. 619c

**Indigosol**, IV. 136b, 113b; VI. 449

O, IV. 129c

**Indigo**, structure and colour, VI. 417a

—, synthetic, VI. 432c

—, manufacture, VI. 441c

—, 5:7:5:7'-tetrabromo-, VI. 452c

**Indigotins**, halogenated, VI. 452c

**Indigotin**, synthetic, VI. 412a

**Indigo**, use of *Cassia tora* with, II. 119b

— White, IV. 135a, 112d, 179d, 185b; VI. 119a

**Indihumin**, VI. 136b

**Indimulsin**, VI. 137c

**Indiretin**, VI. 136b

**Indirubin**, VI. 136b, 438a, 452a, 465b

**Indium**, VI. 457b

— acetylacetone, VI. 160d

— alloys, VI. 158a

— chlorides, VI. 158c

—, defn., II. 593b, 600a

— oxides, VI. 159a

—, qualitative reactions, II. 555b, 569d, 568b

— sulphate, VI. 450d

— trimethyl, VI. 460b

— triphenyl, VI. 160c

**Indocarbocyanines** and indo-2-carbocyanines, I. 577d; III. 519c

**Indocyanines**, I. 577d; III. 519c

**Indole** as perfume, VI. 460d

—, detection and defn., VI. 462d

— from biological material, VI. 462c

— (tryptophan), VI. 462d

— in civet, III. 191b

—, prepn., VI. 462d

**Indoles**, VI. 461a

**Indolignones**, VI. 456b

**$\beta$ -Indolyl-3-acetic acid**, VI. 464a

**Indophenol**, Carbazole, VI. 418c

**Indophenols**, VI. 416c

— as indicators, VI. 417c

—, properties, VI. 417b

**Indothia-**, indoxa-, oxoxazolo-, oxathia- and oxathiazolo-cyanines, III. 522d

**Indotricarbocyanines**, III. 527b

**Indoxyl** and I. compounds, VI. 464c

**Indoxylsulphuric acid**, VI. 465c

**Induction period**, IV. 418d

— in heterogeneous reactions, VI. 223b

**Inductive effect**, VI. 465d

**Inductor**, I. 12c

**Indulines**, I. 579b; VI. 467b

**Indurite**, IV. 465b

**Inflammability** of gaseous mixtures and dust (*see also* Ignition), VI. 427d

**Inflammable mixture**, definition, IV. 427a

**Infusorial earth**, III. 579a

**Ingrain dyes**, IV. 192d, 225b

**Inhibitors**, gum, VI. 469c

—, oxidation, VI. 468d

—, pickling, III. 77a

**Ink**, VI. 485a

—, Chinese, II. 312b; III. 32b; VI. 423c

—, copying, VI. 480d

—, for records, VI. 487a, d

—, hectograph, VI. 490b

—, indelible, VI. 490a

—, Indian, III. 32b; VI. 423c

—, lithographic, VI. 490c

—, marking, VI. 193a

—, powders, aniline, VI. 180c

—, printing, VI. 190d

—, arsenic in, VI. 492d

—, examination, VI. 492d

—, rotography, VI. 492b

—, secret, III. 221b; VI. 489d

—, writing, examination, VI. 488b

**Inosinase**, IV. 315a

**Inosine** in carmine, II. 390d

**Inosinic acid**, VI. 90c

**Inosite**, *see* Inositol.

**Inositol** (*see also* Auxin), VI. 138d, 494a

—, detection and defn., VI. 495d

— in celery, II. 441b

—, yeast, II. 98c

—, mono- and di-methyl ether, II. 32c; III. 546a

**mesoInositol**, VI. 138d, 495a

**Insecticide**, calcium arsenate, II. 220d

—, carbon tetrachloride (*see also* Fumigation), II. 350a

—, catechol, II. 432b

—, emulsions, IV. 301c

—, trichloroethylene, I. 103d

**Insolubles**, treatment, in analysis, II. 550a, 558b

—, pseudo-, treatment in analysis, II. 550a

**Insularine**, VI. 496c

**Insulin**, VI. 496d

—, administration, VI. 501d

—, enzyme action on, VI. 500c

—, molecular weight, VI. 500d

—, physiological action, VI. 500d

—, reactions, VI. 499b

—, standardisation, VI. 502b

—, zinc in, VI. 500a

**Interatomic distances**, VI. 502c

**Interfacial angles**, V. 264a; VI. 506d

**Intermicellar liquid**, III. 284a

**Inukaya** (nugaya) oil, VI. 510b

**Inulase**, IV. 314b

**Inulin**, II. 282b, 286c, 303a

**Inulo-coagulase**, III. 31a

"**Inuar**," VI. 510c

**Inversion** of cane sugar, acid catalysis, II. 530d; VI. 241d

- Invertase** (*see also* Enzymes; Fermentation), II. 76b, 299d; VI. 305a, 510c  
 —, activity detn., VI. 511a  
 —, from moulds, VI. 511c  
**Iodazide**, I. 581b  
**Iodate**, detn., gravimetric, II. 610b  
**Iodates**, qualitative reactions, II. 577b  
**Iodemolite**, II. 481c  
**Iodide**, detn., potentiometric, II. 707c  
**Iodides**, qualitative reactions, II. 577b  
**Iodine**, *see also* Halides; Halogens.  
 — as chlorine carrier, II. 353b  
 — bromide, II. 117a  
 —, compound with casein, II. 414c  
 —, detn., gravimetric, II. 606d  
 —, — in hydrogenation analysis, VI. 302b  
 —, —, potentiometric, II. 707c  
 —, —, volumetric, II. 657c  
 — pentoxide in respirators, III. 21a  
 — reagent for carbon monoxide, II. 351c  
 —, qualitative reactions, II. 577b  
**"Iodised"** salt, I. 506d  
**Iodoform** as disinfectant, IV. 22d  
**Iodyrite**, II. 481c, 516d  
**Ionamines**, I. 39d  
**Ionic** mobilities, definition, VI. 238a  
 — strength, definition, VI. 216a  
**pseudolonone**,  $\alpha$ - and  $\beta$ -, III. 184d  
**Ions**, hydration, VI. 295c  
 —, solvated, VI. 295c, 297d  
**Ipecacuanha**, IV. 280d  
 — alkaloids, *see* Cephaeline; Emetine.  
 —, cephaeline and emetine from (*see also* Emetine), II. 480d  
**Ipecamine**, IV. 281a  
**Ipomoea** spp., I. 655d; VI. 90b  
**"Ipral"**, I. 623a  
**Ipranol**, VI. 90b  
**"Irganaphthol"**, IV. 231a  
**Iridin**, V. 250d; VI. 90c  
**Iridium**, detn., I. 526b; II. 614d  
 —, —, micro-method, II. 633c  
 —, —, qualitative reactions, II. 554d, 556d, 579a  
**Iridosmine**, I. 549d  
**Irigenin**, V. 259d  
**Irish** moss, Irish pearl moss, I. 109b; II. 403c  
 — salt firkin butter, II. 161a  
**Iris**, II. 303b  
**Iris** spp., VI. 90c, 90d  
**Iron** acetate, mordant, II. 53d, 55a  
 —, and manganese, analytical separation, VI. 299b  
 — steel assay, I. 520d  
 — as chlorine carrier, II. 353b  
 — beidellite, I. 663b  
 — boride, II. 44b  
 — carbide, II. 280c, 480c  
 — carbonate, II. 519c  
 — carbonyl, II. 357a  
 — hydride, II. 358a  
**Iron** carbonyl in gases and synthetic methanol, II. 357b  
 — — — town gas, II. 351b  
 — — catalysts in prepn. of higher alcohols, II. 350b  
 — chromium alloy, III. 105b  
 — cyanides, complex, constitution, III. 471d, 473d, 477c  
 —, detn., colorimetric, II. 671c  
 —, —, electrodeposition method, II. 701b  
 —, —, gravimetric, II. 611b  
 —, — in clay, III. 202a  
 —, —, potentiometric, II. 707c  
 — earth, blue-, II. 25b  
 —, electrodeposition, IV. 267a  
 — glance, VI. 160d  
 — in peroxidase, II. 422c  
 — plants, I. 500d; II. 183a, 441d, 487a, 496b  
 — liquid, I. 55a  
 — ore, kidney, VI. 160d  
 — —, micaceous, VI. 160d  
 — oxide, catalyst, action on water gas, II. 349a, 425a  
 —, catalyst in ammonia production, II. 421a  
 —, —, nitric acid manufacture, II. 421c  
 —, — in lacquers, II. 173b  
 —, passive, III. 377a  
 — phosphide, II. 225d  
 —, qualitative reactions, II. 552a, 577d  
 —, —, rare metals present, II. 555a, 556d  
 — salts as disinfectants, IV. 24b  
 —, detn., volumetric, II. 660b  
 —, specular, or specularite, VI. 160d  
 — spinel, I. 261c  
**Irritants** in warfare, III. 7c  
**Irvingia** butter, IV. 1a  
**"Isarit"**, IV. 248c  
**Isatan**, isatase, VI. 136d  
**Isatin**, VI. 463b  
 —, colour reaction with thiophen, VI. 463c  
**Isatis tinctoria**, VI. 90b  
**Isinglass**, V. 510a  
 —, Bengal, I. 162d  
 —, East Indian, II. 102a  
 — finings in beer, II. 102a  
 —, Japanese, I. 162d  
**"Isocaine"**, I. 369a  
**"Isocol"**, III. 515b  
**Isodisperse** sols, III. 289a  
**Isoelectric** point, III. 285b  
**cis-trans-Isomerisation** catalysed by boron trifluoride, VI. 260a  
**Isoprene**, carcinogenic compounds from, II. 378c  
 — from acetylene, I. 85a  
 — in synthesis of 2-methyl-anthraquinone, I. 208b  
 —, polymerides, II. 153c  
 —, prepn., I. 89d; II. 151c  
**Isotetrandine**, II. 481a  
**Isotopes**, *see also* individual elements.  
 —, table, I. 539a  
**Isotopic** equilibria and separations, VI. 220a  
 — exchange, VI. 257b  
**"Istizin"**, I. 222b  
**Itaconic** acid, II. 185d  
 — from fermentation, V. 50d  
**"Itrol"** antiseptic, IV. 26a  
**Ivory**, vegetable, III. 366c  
**Iztactzapotl**, II. 417d

## J

- Jaborandi**, VI. 99c  
**Jacarandin**, VI. 136b, c  
**Jacinth**, VI. 288d  
**Jack** fruit, I. 497d  
**Jacquard** loom, V. 157a  
**Jacqué** test, IV. 534c  
**Jacupirangite**, I. 585b  
**Jaffé** test for creatinine, III. 418a  
**Jaggery**, III. 548d  
**Jalapin**, VI. 90c  
**Jalap** resin, III. 326c  
**Jamesonite**, I. 439d  
**Janus** colours, IV. 210b, 220c  
**Japaconitine**, I. 122b  
**Japonic** acid, II. 438b  
**Jargonelle** pear essence, I. 361c  
**Jasmine** perfumes, synthetic, II. 422a  
**Jateorrhizine**, II. 235b  
**Jatropha curcas**, III. 400c  
**Jatrorrhizine**, II. 235b  
**Jaune** Brilliant, II. 194a  
**Javanine**, III. 128b, 168c  
**Javelle** water, III. 40d  
**Jawar**, II. 482c  
**Jecoleic** acid, III. 217b  
**Jellygraph**, VI. 26a  
**Jequirity**, I. 4c  
**Jeromejefite**, I. 261d  
**Jersey-stone**, III. 32d  
**Jervine**, pseudojervine, VI. 290c  
**Jerwitz** extractor, IV. 582d  
**Jesaconitine**, I. 123a  
**Jesterin**, II. 120c  
**Jesuit's** nut, III. 26d  
**Jigs**, IV. 136b  
**Jørgensen's** method, V. 76a  
**Juglone**, VI. 171b  
**Juniper** (ar oil, II. 188c  
**Juniperus** spp., II. 30d; III. 601b  
**Jute**, II. 461b; V. 163b  
 —, Bmliapatam, V. 164c  
 —, China, V. 164c  
 — hemicellulose and lignin, V. 164b

## K

- Kämpferide**, III. 556c; V. 413b  
**Kämpferin**, III. 556c; VI. 90d  
**Kämpferitrin**, III. 556c; VI. 90d, 439b  
**Kämpferol**, III. 556a; VI. 90d, 439b  
 — rhamnoside, III. 556c  
**Kaffir** corn, II. 482c  
**Kaffirin** in millet, II. 481b  
**"Kahweol"**, III. 257d  
**Kaijo**, V. 94a  
**Kainit**, kainite, II. 109b; V. 74b  
**Kajoo**, I. 365d  
**Kakodyl**, I. 480a  
**Kalanite**, I. 703d  
**Kale**, II. 182b; III. 432d  
**Kaliborate**, II. 35b  
**Kalinite**, I. 204c; IV. 591d

- Kalioalunite**, I. 298a  
**Kalkstickstoff**, V. 65d  
*"Kalmopyrin"*, I. 370a  
**Kanswe** (Kansive) Oil, I. 655a  
**Kanya** butter, II. 168d  
**Kaolin** (*see also* Clay), III. 195d  
**Kaolinite**, I. 264d; III. 196a  
**Kapok**, kapok oil, V. 168c; III. 411, foot-note  
**Karasu-urî** seed oil, IV. 86d  
**Karité** butter, I. 654b  
*"Karitene"*, I. 653d  
**Karystian** stone, I. 500b  
**Karystiolite**, I. 500b  
**Kast** brisance test, IV. 519c  
**Katanols**, IV. 132a  
**Katathermometer**, VI. 288b  
**Kath**, II. 433c  
**Katharometer**, VI. 286b  
**Katio** oil, I. 655a  
**Katsuobushi**, V. 59c  
**Kavatel** oil, II. 522d  
**Kayene**,  $\alpha$ - and  $\beta$ -, I. 160d  
**K.C.U.**, or kilogram-centigrade unit, V. 331c  
**Keaving** in cedar, III. 125c  
**Kekin**, kukui or kekua oil, II. 202c  
*"Kelene"*, IV. 359a  
**Keller-Kiliani** reaction, II. 383d  
**Kellner** electrolytic cell, III. 55d  
*-Solvay* electrolytic cell, III. 56b  
**Kelp**, I. 199a  
**Kelvin** temperature scale, VI. 412b  
**Kemps** in wool, V. 98a  
**Kentallinite**, V. 109b  
**Kephalin**, brain, and thiom  
 kokmase, II. 23d  
*-*, colamine from, III. 94a  
**Kephalins** from brain and soya bean, II. 54a; VI. 70a  
**Keracynin**, I. 449a; III. 25c; VI. 90d  
*"Keramyil"* disinfectant, IV. 23a  
**Kerasin**, II. 506c; VI. 90d  
**Keratin**, II. 12c  
*-*,  $\alpha$ - and  $\beta$ -, V. 102b  
*"Keratin"* in plasters, II. 131c  
**Keratins**, IV. 123a; VI. 21b  
*"Kermes* by the dry way," I. 446d  
**Kermesite**, I. 439d, 440d  
**Kermes**, kermesic acid, III. 226b  
*-* mineral, I. 446c  
**Kerner** test for cinchonidine, III. 133d  
**Kernite**, II. 40a, 49a  
**Késú**, II. 157d  
**Kesuda**, II. 157d  
**Keten** acetals, I. 36d  
*-* from acetaldehyde, I. 25a  
*p*-**Ketobornyl** chloride, II. 252b  
**Ketocamphor**, II. 240c  
 *$\beta$ -Ketoesters*, alkylation, II. 367d  
**Ketols**, I. 30c  
**Ketones**, II. 373c  
*-*, compounds with sugars, II. 290a  
*-* from carbon monoxide, II. 350b  
*-*, halogenation, VI. 257b  
*-*, oxidation, II. 362b  
*-*, prototropy, VI. 256c  
**Ketopinic** acid, II. 33c  
**Ketoses** from aldoses, II. 293d  
**Keweenawite**, IV. 55c  
**Khakan** fat, III. 244b  
**Khaki**, Indanthrene, 2G, 1. 422b  
*-* shades, IV. 127c  
*"Kharsivan"*, I. 491b  
*"Kharsulphan"*, I. 492a  
**Kier** boil in cotton bleaching, II. 3d, 6d; V. 184a  
**Kiers**, II. 6b  
**Kieselguhr**, III. 579a; IV. 230b  
**Kieserite**, IV. 321b  
**Killas**, VI. 120c  
**Kilns**, Hofman, zig-zag, II. 124c  
**Kimberlite**, III. 575d  
*"Kineurine"*, III. 174a  
**King** extractor, IV. 582c  
**Kino**, Bengal, II. 157d  
**Kirschner** value of butter, II. 166a  
**Kirschwasser**, III. 25a  
**Kish**, II. 315a  
**Kitul**, V. 168b  
**Kjeldahl** - Gunning nitrogen detn., II. 83b  
**Kjeldahl** nitrogen detn., II. 619b; IV. 602a  
*- - -*, micro-method, II. 631c  
**Kliachite**, I. 650d  
*"Klimakone"*, IV. 52c  
**Knight** packet sampler, I. 519a  
**Knochenöl**, II. 29d  
**Knock** in petrol-air engines, IV. 142c, 144a, 449a  
**Knorr** extractor, IV. 577a  
**Kochelite**, II. 512c  
**Kochite**, I. 261d  
**Kodachrome**, Kodacolor processes, II. 446d, 453a  
**Königswasser**, I. 153b  
*"Kogasin"*, I. and II., V. 378c  
**Koh-i-noor**, III. 578a  
**Kohl**, VI. 170d  
*-* -rabi, II. 182b  
**Koji**, V. 59b  
**Kojic** acid from *Aspergillus oryzae*, V. 51d  
**Kokaro**, II. 264b  
**Kokusagine**, III. 602d  
**Kola** nuts, theobromine in, II. 197c  
**Kolatein**, II. 438d  
**Kolbe** reaction, II. 364b  
*"Kolchugalamit"*, I. 253b  
**Koller** grate, V. 371b  
**Konjak** powder, glucomannan in, II. 302d  
*"Koroseal"* plastic, I. 91d  
**Koumine**, kouminine, kouminidine and kouminne, V. 511a  
**Kounidine**, V. 511b  
**Kousso**, III. 463c  
**Kou-wen**, V. 511b  
**Krabao** oil, II. 521d  
**Kraft** paper, II. 462a  
**Kraut** reagent, I. 235c  
**Krebs** electrolytic cell, III. 54b  
**Kreis** test for almond oil, I. 200c  
*-* - - - rancidity, II. 108b  
*"Kronelyne"* (T.P.P.), I. 263d  
**Kryptocyanine**, III. 517c  
**Krypton**, detn., spectroscopic, II. 092a  
**Kryptopyrrole**, III. 83b  
**Kryptoxanthin**, II. 272b, 309c; III. 184d  
*"KrySTALLIN"*, I. 372c  
**K. S. Seewasser** (K.S.S.) alloy I. 251c, 275b, 277c  
**Kukoline**, IV. 52d  
**Kunstlab**, IV. 315c  
**Kupferblende**, IV. 500d  
**Kupfernickel**, I. 469a  
**Kupferpfecherz**, III. 119b  
**Kupfer-smaragd**, IV. 7d  
**Kupramite**, in respirators, III. 20c  
**Kurchenine**, III. 323c  
**Kurchi-bark**, alkaloids, III. 321d, 324a  
**Kurchicine**, kurchine, III. 323c  
**Kuromame**, III. 110a  
**Kusu** oil, IV. 4b  
**Kutch**, I. 11c  
**Kyanite**, I. 261d, 370b  
*"Kyanol"*, I. 372c  
**Kynoch** smokeless powder, IV. 519b

## L

- Labradorite**, I. 652a; V. 3a  
**Laccase**, IV. 315b  
**Lachrymators** in warfare, III. 7c  
**Lacquers**, *see also* Acaroid resins; Cellulose lacquers; Dammar resin; Cellulose, II. 467d  
*-*, cold, II. 469c  
*-*, greening, II. 473b  
*-*, nitrocellulose, II. 464b  
**Lactacidogen**, V. 24c; VI. 75a  
**Lactalbumin**, II. 412c  
**Lactase**, II. 299b; IV. 282d  
**Lactic** acid fermentation, V. 50d  
*-* formation in muscle extract, V. 31c  
*-* in brain, VI. 70b  
*-* food, detection and detn., V. 300a  
*-* - - - muscle extract, V. 31c, 34d; VI. 74d, 75c  
*-* bacteria in brewing, II. 87a  
*-* - - - butter, II. 160a  
**Lactobacillus acidophilus**, I. 43d  
**Lactoflavin**, I. 199c; II. 287b; VI. 91a  
**Lactose**, II. 282b, 298b, 299a  
*neo*Lactose, II. 299b  
**Lactulose**, II. 299b  
**Laderellite**, II. 35b, 48b  
**Lævoglucosan**, II. 295b  
**Lævulinic** acid and derivs. (*see also* Lævulinic acid), I. 71d  
**Lævulinic** or lævulic acid, II. 288c  
**Lævulose**, *see also* Fructose  
*-* in cabbage, cereals, II. 183a, 487a  
**Lake**, definition, IV. 128b  
*-* dyes, III. 335c, 336a; IV. 234c  
**Lakes** in plastics, II. 476b  
**Lallemantia** oil, IV. 86c  
**Lama huanaco**, I. 202d  
**Laminarin**, I. 199c  
**Lampblack**, II. 312a; VI. 423c  
**Langmuir's** equation, VI. 373a  
*-* isotherm, II. 540a; VI. 208c, 209d, 217a

- "*Lanital*," II. 416a; IV. 125c; V. 113d  
**Lanolin**, III. 92c  
**Lanosterol**, III. 92d  
**Lanthanum** in cerite, II. 507a, 511c  
 — nitrate in ash detns., II. 83a  
**Lanthocerite**, II. 507a  
**Lap**, V. 145b  
**"Lapis"**, German and Swiss, V. 514c  
**Lapis-lazuli**, I. 291c; V. 514c  
**Lappaconitine**, I. 123c  
**Lard oil**, VI. 135a  
 — substitutes, IV. 253b  
**"Largin"**, antiseptic, IV. 26a  
**Larkspur**, alkaloids, III. 550c  
**Larocaine**, I. 369a  
**Lasne method**, V. 79a  
**Lassaigne's test** for nitrogen, II. 615a  
**Lateralisation**, of granitic rocks, III. 194d  
**Laterite**, I. 650c  
 —, building stone, II. 138i  
**Latex**, uses, for textiles, V. 191d  
**Latifolia fat**, I. 653a  
**Laughing gas**, I. 367a  
**Laurasin**, III. 20a  
**Laurent acid**, IV. 206d  
**Laurin** in Cáy Cáy fat, II. 439c  
**Laurite**, III. 327c  
***Laurocerasi folia*** (B.P.), III. 26a  
**isoLaurolene**, II. 248d  
**Laurolic acid**, lauronolic acid, II. 249a  
 **$\gamma$ -Lauronolic acid**, II. 249a  
**isoLauronolic acid**, II. 218b  
**Laurvikite**, V. 409a  
**"Lautal"**, I. 253b, 277a  
**Lautarite**, III. 601a  
**"Lawsons"**, VI. 171b, 201d  
***Lausonia alba***, I. 236d; VI. 204c  
**Lazulite**, I. 583d  
**Lazurite**, I. 201d, 583d  
**Leaching**, IV. 502d  
**Lead acetylide**, II. 281c  
 — as trace element, I. 507b  
 — block test, IV. 517d  
 — burning, oxy-acetylene, I. 116c  
 — carbonate, II. 516d  
 — chromate, III. 96d, 111d  
 —, mineral, III. 430a  
 — cyanate, III. 507c  
 —, detn., assay, I. 527b  
 —, — by electrodeposition, II. 701b; IV. 268d  
 —, —, colorimetric, II. 671d  
 —, —, gravimetric, II. 596b  
 —, in food, II. 292c; V. 292c  
 —, — water supplies, II. 292c  
 —, —, potentiometric, II. 707d  
 —, —, volumetric, II. 661b  
 —, drop reaction, II. 580c  
 — nitrate explosives, IV. 404c  
 — oxychloride, II. 418b  
 — poisoning in ceramic industries, VI. 6c  
 —, qualitative reactions, II. 551a, 571c  
 —, —, rare metals present, II. 554b, 556d  
 —, red, and litharge for glass-making, V. 561b  
 — stearate in candles, II. 264d  
 —, sugar of, I. 55b  
 — sulphantimonite, II. 53d  
 — **d tetraisobutyl**, II. 173c  
 tetraethyl, IV. 417d  
 —, detn., II. 684a  
 — tin alloys, electrodeposition, IV. 270c  
**Leaf beetle**, II. 520c  
**Leather**, artificial, V. 195c  
 —, casein in finishing, II. 414b  
 — cloths, V. 195b  
 — degreasing by trichloroethylene, I. 103a  
 — finishing, castor oil in, II. 422a  
**Leaven**, II. 79b  
**Lebedev extract**, V. 14a  
**Leblanc process**, III. 69d  
**Leblelji**, III. 20b  
**Le Chatelier-Braun equilibrium**, II. 534d, 538a; VI. 229b  
**Lecithide** in rice, II. 499a  
**Lecithin**, VI. 70a  
**Lecithinase**, IV. 314b  
**Lecithin** in foods, II. 186a, 499a; III. 87c  
**Ledger** (cinchona) bark, III. 128b  
**Ledouxite**, IV. 55c  
**Légal reaction**, of cardiac glycosides, II. 383d  
**Legumes**, III. 432c  
**Lemon Chrome**, III. 112b  
 — grass oil, citral in, III. 183d  
 — juice, III. 186d  
**Lena Batu**, III. 191a  
**Lepargylic acid**, I. 561c  
**Lepidine**, III. 159b  
**Lepidocrocite**, II. 25d; VI. 101b  
**Lepidolite**, II. 195c  
**Leptocine**, III. 323d  
**Leucauramine**, I. 548c  
**Leucine**, carbamic acid from, II. 278b  
**d-isoLeucine**, l-leucine, I. 317c  
**Leucite**, I. 261d, 652a  
 — nepheline-tephrite, I. 4c  
**Leucoalizarin**, I. 210d  
**Leucoaposafranine**, I. 574d  
**Leucocytes**, of blood, II. 19d  
**Leuco-indigoid dyes**, VI. 451d  
**Leucopyrite**, I. 469a  
**Leucoquinizarin**, I. 221b  
**Leucosin**, II. 505a  
**"Leunaphos"**, I. 353d  
**"Leunasalpetar"**, I. 352d  
**Levan**, II. 303b  
**Libethenite**, III. 359a  
**Lichenase**, II. 87d  
**Lichenin**, acetolysis, II. 442d  
**Lichtenberg's alloy**, I. 698d  
**Lichtenecker's formula**, V. 546b  
**Lichtnussbaum**, II. 262c  
**Liesegang's rings**, III. 293c  
**Lievrite**, VI. 415b  
**Ligninsulphonate**, calcium, II. 461d  
**Lignites**, V. 338c  
**Lignocellulose**, II. 407a  
**Lignoceric acid**, I. 450a; II. 390b  
***Lilium tigrinum***, I. 381b  
**Lily of the valley**, glycosides, II. 387a; III. 326c  
**Lima wood**, II. 68a  
**Lime and limestone for glass-making**, V. 560b  
 —, basic carbonates from, II. 221c  
 —, Blue Lias, II. 193d, 210d  
**Lime boil**, II. 5d; V. 183d  
 —, **Chaux de Teil**, II. 210b  
 — deficiency in grass land, VI. 132d  
 —, free, detn., II. 654c  
 — (fruit) juice, III. 186d  
 —, ground, II. 135b  
 — in building materials, II. 133a  
 — casein paints, II. 415c  
 —, milk of, II. 212a  
 — production and uses, II. 206b  
 —, reaction with carbon monoxide and steam, II. 349b  
**Limes**, "fat" and "poor," II. 210d  
 —, grey, II. 133c  
**Lime**, slaking, for building, II. 134b  
**Limes**, magnesian, II. 135c; IV. 54a  
**Limestone** as building stone, II. 137c  
 — for glassmaking, V. 560c  
**Limonene**, autoxidation, II. 404d  
 —, degradation to isoprene, II. 154d  
 —, nitroso-, II. 407a  
**Limonite**, II. 20a  
**Linalol**, see Linalool.  
**Linalool** in coriander oil, III. 364d  
 — in essential oils, I. 684a; II. 249c, 261b; III. 183b, c, 364d  
 —, prepn., V. 517d  
**Linamarin**, VI. 91a  
**Linarin**, VI. 91b  
**Linene**, bleaching, II. 11a  
**Linnaite**, III. 214b, 222c  
**Linoleates** in boiled oil, I. 25b  
**Linoleic acid**, I. 190c  
 — — — glycerides (see also Drying oils), II. 163a, 263a, 421b, 494b; VI. 68d  
**Linolenic acid** glycerides, see Drying oils.  
 — — — occurrence, II. 237b, 263a  
**Linolic acid**, see Linoleic acid.  
**Linoplastic**, II. 475d  
**Linotype metal**, I. 445c  
**Linoxyn**, II. 25a  
**Linseed cattle-cake**, I. 455a; IV. 594c  
 — oil, bleached, IV. 88a  
 — — — "break," IV. 87c  
 —, refining, IV. 87c  
 —, stand oil, IV. 88c  
 —, substitutes, IV. 81d, 87b  
 —, sulphurised, IV. 90c  
 —, theory of drying process, IV. 92b  
**Linters**, III. 409c; IV. 506b; V. 116c, 135d  
**Liparite**, III. 32d  
**Lipase** in castor oil seeds, II. 420b  
 — — — malting, II. 89a  
 — — — rice, II. 495d  
**Lipases**, IV. 313b; VI. 395b, 396d  
**Lipochrome**; lipid ratio, II. 394a  
**Lipochromes**, II. 397d  
**Lipowits's alloy**, I. 698c  
**Liquation**, IV. 276d  
**Liqueurs**, III. 361b  
**"Liquid carbolic acid"**, III. 426b



**Liquiritin**, VI. 91b  
**Liquor cresolis saponatus**, IV. 29b  
 — *plumbi subacetatis*, I. 55c  
 — *Lissolamine*, IV. 145d  
**Lister's salt**, IV. 25d  
 — *"Lithiopyrin"*, I. 453b  
**Lithium** carbonyl, II. 357c  
 —, detn., gravimetric, II. 583c  
 — in feranite, II. 393b  
 — occurrence in plants, I. 507c  
 —, qualitative reactions, II. 547c, 556c, 563d, 565d  
**Lithocholic acid**, I. 689b  
**Litho oils**, IV. 88c; VI. 491a  
**Lithopone**, I. 840d  
 — in moulding powders, II. 479b  
**Lithothamnium**, coral from, III. 360b  
**Litmus**, II. 640b  
**Little's** "soluble phenyle," IV. 29d  
**Liver** esterase, inhibition, II. 200c  
 — extract, VI. 204d  
 — oil, Suketodara, III. 244c  
**Livetin**, IV. 255d  
**Llisteria**, V. 328c  
 — *"Locron"*, V. 226a  
**Löllingite**, I. 409a  
**"Lo-Ex"** ("Loex") alloy, I. 253b, 277c  
**Logwood**, II. 237b; IV. 126a  
**Lohmann's** esters, V. 24d  
**Lopionic acid**, III. 141c, 160a  
**Longifolia** fat, I. 653b, foot-note  
**Lonicera** spp., VI. 265c  
**Loonzein**, II. 490b  
**Lophine**, VI. 99a  
 —, luminescent oxidation, III. 21a  
**"Lopion"**, VI. 119b  
**Loranskite**, II. 512c  
**"Lords and Ladies"**, I. 497d  
**Lorentz** and Lorenz formula, V. 546b  
**"Lorol"**, IV. 286b  
**Loturine**, VI. 188a  
**Lotus arabicus**, VI. 91b  
**Lotusin**, VI. 91b  
**Lowe's** test, of phenol, II. 304c, 308b  
**Low-temperature** carbonisation, V. 364d, 450a  
 — "low wines," V. 532d  
**L.O.X.**, IV. 546a  
**Lubanol**, I. 615d  
**Lubricants**, carcinogenic, II. 378b  
 —, castor oil in, II. 420c  
 —, refining, II. 308d  
**Lubrication**, boundary, VI. 509a  
**Lucerne**, I. 199a  
 — meal, IV. 596b  
**Luciculine**, I. 124a  
**Lucidusculine**, I. 123d  
**Luciferase**, luciferin, III. 24a  
**Lukrabo** oil, II. 521d  
**Lulu-butter**, I. 654b  
**Lumbag**, candle-nut oil, I. 198c; II. 262b; IV. 83d  
**Lumbricus**, hæmoglobin, VI. 165c  
**Lumen**, definition, V. 171d, foot-note  
**Lumiflavin**, relation to vitamin B<sub>2</sub>, II. 287b

**"Luminal"**, I. 623a  
**Lumisterol**, II. 202a; IV. 326d  
**Lupeol**, I. 653d  
**Lupinus** spp., I. 459b; VI. 89b  
**Lupulon**, II. 92a  
**Lupus metallorum**, I. 446b  
**Lusitanicoside**, VI. 91c  
**Lussatite**, II. 517b  
**Lutecia**, II. 480b  
**Lutecite**, II. 517b  
**Lutecium** metals, II. 511c  
**Luteic acid**, V. 58a; VI. 91c  
**Lutein**, I. 201a; II. 272b, 398a; III. 184d  
**Luteoleersin**, V. 56d  
**Luteolin**, IV. 189a  
**Luteolinidin**, V. 253a  
**Lutose**, V. 58a  
**Lutidine** from acetylene, I. 84c  
**Luxullianite**, VI. 127b  
**Luzonite**, IV. 308a  
**Lycacotinins**, I. 123d  
**Lycine**, I. 680a  
**Lycopenal**, II. 399b  
**Lycopene**, II. 398a  
**Lycoperdin**, lycoperdon, VI. 91c  
**Lycophyll**, II. 399d  
**Lycoxanthin**, II. 399c  
**Lyddite**, II. 308d; IV. 476d  
**Lydian-stone**, I. 4b  
**Lynn** washer, V. 495  
**Lymph**, physiology, II. 21a  
**Lynite**, I. 277c  
**Lyophilic** colloids, III. 279d  
**Lyophobic** colloids, III. 279d  
**Lyotropic** series, III. 286d  
**Lysergic acid**, IV. 328a  
**Lysine** in cabbage, II. 182d  
**"Lysol"**, III. 427d; IV. 20b, 33d  
**Lysolecithin**, II. 499a  
**Lysozyme**, IV. 255b  
**"Lytophan"**, VI. 226b

M

**"Macarite"**, IV. 464c, 465d  
**Machilol**, IV. 393a  
**Machilus kusanoi**, machilol from, IV. 393a  
**Maclagen's** test for cocaine, III. 224b  
**Macoubeine**, III. 400c  
**Madara** oils, III. 240c  
**Madder**, I. 203b; IV. 126c  
 —, Indian, II. 523c  
**Madhuca** spp., I. 653a, c, 654a  
**Magenta**, Acid, I. 120a  
**"Magnalium"**, I. 253b, 277c  
**Magnesia**, caustic, II. 136b  
 —, dead-burnt, II. 136b  
 — for glassmaking, V. 560c  
 — in calcium carbide manufacture, II. 217a  
**Magnesian** limestone, II. 135c; IV. 54a  
**Magnesite**, decomposition, II. 324c  
**Magnesium** acetate in flour analysis, II. 83a  
 —, action on prothrombin, II. 23c  
 — alloys, I. 255b  
 — and its alloys, protection, III. 393a  
 — as trace element, I. 507c

**Magnesium** boride, II. 41a, 44b  
 — carbide, II. 281b  
 — chloride in carnallite, II. 390a  
 — chloroborate, II. 30b, 48d  
 — compounds in building materials, II. 128b, 133a  
 — cyanide, III. 402b  
 —, detn., colorimetric, II. 671d  
 —, gravimetric, II. 588a  
 —, in clay, III. 203b  
 —, spectroscopic, II. 692a  
 —, volumetric, II. 661d  
 drop reaction, II. 580d  
 — hydrosilicate, adsorbent, IV. 248b  
 — hydroxide, mineral, II. 119b  
 — ions, catalytic effect in muscle extract, VI. 77d  
 — oxide, action on water gas, II. 349b  
 — oxychloride cement, II. 135c  
 —, qualitative reactions, II. 551a, 567a  
 —, rate metals present, II. 556c, 563a  
 — uranyl acetate, II. 584b  
**Magneson** test for Mg, II. 556c  
**Magnetite**, II. 393b  
**"Magnuminum"**, I. 255d  
**Magney** libre, V. 167d  
**Maha** pengiri grass, citronella oil from, III. 191a  
**Mahua** butter, I. 653a  
**Ma Huang**, IV. 316c  
**Maitrank**, III. 412d  
**Maiuri** dry ice process, II. 327b  
**Maiwein**, III. 412d  
**Maize**, II. 481d  
 —, detn. in wheat, II. 482a  
 — oil, II. 482c  
 — starch, fermentation, II. 471d  
**Maja squinado**, astacin from, I. 532c  
**Malachite**, III. 26c, 341c, 355d  
**Maladie de la tournee**, III. 127a  
**Malates**, qualitative reactions, II. 570a  
**Male** fern, V. 180d  
**Maleic acid**, V. 387a  
 — anhydride, addition to dienes, II. 152d  
 —, prepn., II. 428a  
 —, reactions, V. 388b  
**Maleyl** chloride, V. 387b  
**Malic acid** from mould fermentation, V. 50c  
 —, prepn., II. 428a  
**Malinowskite**, IV. 590d  
**Malladrite**, V. 60b  
**Malolalic acid**, I. 451b  
**Malonhydroxamic acid**, II. 352d  
**Malonic acid** formation, II. 352d  
 — amide, II. 352d  
 — anhydride, *see* Carbon suboxide  
**Malonyl** chloride, II. 352d  
**Malonylurea**, I. 620c  
**Malt**, *see* Amylase; Barley; Brewing  
 — extract (*see also* Amylase), I. 645b  
**Maltase**, action on maltose, II. 299a  
 — in dough, II. 76b  
**Maltng**, II. 87b

- Maltodextrin** and maltodextrin- $\alpha$  and  $\beta$ , III. 508*d*, 569*a*  
 "Maltodextrin" from conc. starch solutions, III. 569*b*  
 $\gamma$ -Maltodextrin, III. 569*a*  
**Maltose**, II. 282*b*, 298*b*  
 — units in starch, II. 301*c*  
**Malvidin**, III. 554*c*  
 — monoglucoside, I. 357*c*  
**Malvin**, III. 554*c*; VI. 91*d*  
**Marneli's** extractor, IV. 588*c*  
**Manamylin**, IV. 275*b*  
**Mancona** bark, IV. 335*d*  
**Mandelic** acid, antiseptic, IV. 29*b*  
**Mandelonitrile**, I. 357*d*  
 —  $\beta$ -glucoside, I. 357*d*  
**Mandoc** starch, II. 418*c*  
**Manelresene**, IV. 275*b*  
**Manganaxinite**, I. 540*d*  
**Manganbrucite**, II. 119*b*  
**Manganese** aluminate, V. 414*b*  
 — and iron, analytical separation, VI. 299*b*  
 — borate in boiled oil, II. 26*b*  
 — boride, II. 44*b*  
 — carbide, II. 281*c*  
 — deficiency disease, II. 507*c*  
 —, detn., assay, I. 527*d*  
 —, —, colorimetric, II. 672*a*  
 —, —, electrodeposition, II. 701*c*  
 —, —, gravimetric, II. 610*b*  
 —, — in clay, III. 202*d*  
 —, —, — water supply, V. 292*d*  
 —, —, volumetric, II. 602*a*  
 — in rice, II. 406*b*  
 — wheat, II. 505*c*  
 — oxide, action on carbon monoxide, II. 350*d*  
 —, —, hydrated, III. 214*c*  
 —, — in respirators, III. 19*b*  
 —, oxides, mineral, II. 119*a*  
 —, peroxide, oxidation of carbon monoxide by, II. 317*a*  
 —, qualitative reactions, II. 548*a*, 552*b*, 577*c*  
 —, —, rare metals present, II. 555*d*, 556*d*  
 —, —, separations, II. 553*c*  
 —, trace element, II. 505*c*, 507*c*  
**Manganite**, III. 579*a*  
**Manganocolumbite**, III. 309*c*  
**Mangel-wurzel**, I. 661*c*  
**Mangold**, I. 661*c*  
**Manila**, II. 461*b*  
 — elemi, IV. 275*a*  
**Mannan**, II. 403*a*; VI. 201*a*  
**Mannanase**, IV. 314*b*  
**Mannan** in carob fruits, II. 393*b*  
**Mapnans**, II. 302*d*  
**Manninotriose**, II. 301*b*  
**Mannite** in cabbage, II. 183*a*  
 $d$ -Mannite, II. 269*c*  
**Mannitol**, II. 296*c*  
 —, formation, II. 285*b*  
 — from moulds, V. 51*c*  
 —, hexanitro-, IV. 500*d*  
 — in celery, II. 441*b*  
 —, —, ergot, IV. 331*d*  
**Mannobiose** from mannans, II. 302*d*  
**Mannocarolose**, V. 58*a*  
 $d$ -Mannoketoseptose, II. 286*d* \*  
**Mannose**, II. 282*b*, 403*a*  
 — in carob fruits, II. 403*a*  
**Mannoside**, VI. 82*c*  
**Mannuronic** acid, II. 297*d*  
 "Manucol," V. 124*d*  
**Manure**, farmyard, V. 61*b*  
 —, fish, V. 61*b*  
 —, seaweed, V. 61*b*  
**Manures** (see also Fertilisers), V. 61*a*  
 —, relative value, V. 74*b*  
 "Mapharsen," I. 489*b*  
**Maraschino**, III. 25*a*  
**Marble**, building, II. 137*c*  
**Marc**, II. 63*c*  
**Marcasite**, III. 327*c*  
**Margarite**, IV. 279*d*  
**Margosa** bark, M. oil, I. 561*a*  
**Marine** glue, VI. 21*b*  
 — soaps, III. 212*b*  
**Marinobufagin**, II. 388*c*  
**Marinobufotoxin**, II. 388*c*  
**Markasol**, I. 700*d*  
**Marmelosin**, I. 155*c*  
**Maroon**, Ahzarim, I. 228*c*, 303*b*  
**Marotti** oil, II. 523*b*  
**Marsh** mallow, I. 263*d*  
**Marsh's** test, I. 470*c*  
**Marua**, II. 482*d*  
**Marver**, V. 578*c*  
**Mash** in brewing, II. 91*d*  
**Mass** action law, II. 533*c*, 536*b*; IV. 338*b*; VI. 383*a*  
**Mastic** in lacquers, II. 409*d*  
**Mastodambrose**, VI. 491*c*  
**Matosano**, II. 117*d*  
**Matte**, cobalt, III. 214*d*  
 —, copper, III. 342*c*  
**Matteucinol**, V. 253*a*  
 "Mauve," I. 577*c*  
**Mauveine**, I. 561*c*, 570*b*, 577*b*  
 "Maxochlor," III. 64*c*  
**Mayer's** reagent, J. 235*d*  
**Mayonnaise**, IV. 303*b*  
**Mead**, VI. 261*b*  
**Meadow** saffron seeds, colchicine from, III. 276*b*  
**Meal**, bone, IV. 597*b*  
 —, —, as feeding stuff, IV. 597*c*  
 —, fish, IV. 597*b*  
 —, meat, IV. 597*b*  
 —, — and bone, IV. 597*b*  
**Mecocyanin**, VI. 91*d*  
**Medicago** spp., I. 199*a*; III. 205*c*  
 "Medinal," I. 623*a*  
**Mee** oil, I. 653*c*  
**Megass**, I. 585*d*  
**Meller** oven, II. 310*c*  
**Meker** burner, V. 250*c*  
**Mekocyanin**, relation to cyanidin, III. 116*a*  
**Melaconite**, III. 341*c*, 354*b*  
**Melamine**, III. 603*b*  
**Melanchroite**, chromium in, III. 90*b*  
**Mel depuratum**, VI. 264*b*  
**Melezitose**, II. 282*b*, 301*c*  
**Melia azadirachta**, I. 561*a*; V. 510*a*  
**Melibiose**, II. 209*c*  
**Melibiose**, II. 208*b*, 209*c*  
**Melilite**, I. 652*a*  
**Mellitic** acid, III. 412*c*  
**Mellilotin**, III. 412*d*; VI. 91*d*  
**Mellitoside**, VI. 91*d*  
**Melinite**, IV. 476*d*  
**Melissyl** alcohol in rice, II. 494*b*  
 — cerotate, in rice, II. 494*b*  
**Mellein**, V. 53*a*  
**Mellite**, I. 264*d*  
**Mellitic** acid, II. 310*c*  
**Melting-point**, incongruent, VI. 415*d*  
**Mendozite**, I. 296*a*  
**Mengrite**, II. 512*b*  
**Menhaden** oil, V. 227*b*  
**Menthadiene**, II. 405*a*  
 — in chenopodium, III. 24*d*  
**Menthol**, prepn., II. 426*d*  
**Mercaptan**, II. 084*a*  
**Mercaptans**, formation in wood-pulping, II. 462*a*  
**Mercerisation** methods and plant, V. 143*b*, 184*a*  
**Mercerising** and parchmentising, V. 191*b*  
 — cotton cloth and yarn, IV. 122*d*, 130*d*; V. 184*a*  
 —, — rayon fabrics, V. 186*a*  
 —, effect on fibre structure, II. 406*c*  
 — in viscose manufacture, I. 117*d*; II. 342*d*, 465*b*  
**Mercuration** of chichona alkaloids, III. 135*b*  
**Mercuretol**, I. 162*b*  
**Mercuri-acetaldehyde**, trichloro-, I. 16*c*  
**Mercuric** compounds, see also Mercurium.  
 — cyanide, III. 487*a*  
 — oxide, oxidation of aldehydes by, II. 362*b*  
 — salts, qualitative reactions, II. 567*d*  
**Mercurius silac** I. 418*a*  
**Mercurochrome**, IV. 316*c*  
 "Mecurophen" antiseptic, IV. 25*d*  
**Mercurous** compounds, see also Mercury.  
 — chloride, II. 235*a*  
 — salts, qualitative reactions, II. 567*d*  
**Mercury** carbide, II. 281*b*  
 — compounds, see also Mercuric and Mercurous compounds.  
 —, detn., assay, I. 528*a*  
 —, — by hydrogenation, VI. 361*d*  
 —, —, electrodeposition, II. 701*d*  
 —, —, gravimetric, II. 590*d*  
 —, — in gases, II. 684*a*  
 —, — hydrogenation analysis, VI. 362*a*  
 —, —, potentiometric method, II. 707*d*  
 —, —, volumetric, II. 662*c*  
 —, drop reaction, II. 580*d*  
 —, electrodeposition, IV. 270*a*  
 — fulminate, action of metals on, IV. 540*a*  
 —, Chandelon's process, IV. 538*c*  
 —, Chevalier's process, IV. 536*b*  
 —, detn. of carbon and nitrogen, IV. 542*b*  
 —, — oxalate, IV. 542*a*  
 —, — total and free mercury, IV. 541*c*, 542*a*  
 —, effect of conditions, IV. 538*d*, 539*d*  
 —, explosive properties, IV. 540*b*, 542*b*  
 —, —, relative value, IV. 541*c*  
 —, properties and density, IV. 538*a*  
 — manufacture, IV. 537*b*

- Mercury** fulminate, physiological effects, IV, 541c  
 --, tests, IV, 541c  
 --, qualitative reactions, II, 551a, 567d  
 --, --, rare metals present, II, 554d, 556d  
 -- salts, reaction with iron carbonyl, II, 358b  
 -- sulphide, II, 179c  
**Meriodin**, I, 380d  
**Meroquinene**, III, 140b, 150c  
**Merrill - Crowe** process, VI, 106c  
**Mesabite**, VI, 101b  
**Mesaconitine**, I, 121c, 122c, d  
**Mesidine**, I, 573b; III, 458a  
**Mesitylene**, I, 66d, 460d; III, 157c  
**Mesityl oxide**, I, 66d  
**Mesobilirubin**, mesobilirubinogen, I, 691a, d  
**Mesocystine**, III, 512b  
**Mesomeric** effect, VI, 406b  
**Mesomerism**, VI, 251a, 257a, 466a  
**Mesoporphyrin**, III, 83a; VI, 162b  
 --, synthesis, II, 20d  
 -- "*Mesotan*," IV, 333b  
**Mesoxalylcarbamide**, I, 243d  
**Metaboric acid**, II, 47d  
 -- formation, II, 17a  
**Metabutaldehyde**, II, 157a  
**Metachloral**, III, 35b  
**Metacinnabarite**, III, 180a  
**Metacristobalite**, III, 428c  
 -- "*Meta*" fuel, I, 26b  
**Metafulminuric acid**, V, 385d  
**Metaheawettite**, VI, 224d  
**Metal argentum**, I, 445d  
 -- chlorides, reduction, II, 360c  
 -- cleaning by trichloroethylene, 102c  
**Metaldehyde**, I, 21b, 26a  
**Metal-hydrogen** alloys, VI, 319c  
**Metals**, defn., *see also* Assaying.  
 --, --, colorimetric, II, 669b  
 --, --, electrodeposition, II, 695c  
 --, --, gravimetric, II, 583c  
 --, --, potentiometric, II, 702d  
 --, --, spectroscopic, II, 690b  
 --, --, volumetric, II, 650b  
 --, drop reactions, II, 579c  
 --, micro-defn., II, 633b  
**Metal-spraying**, oxy-acetylene, I, 116d  
**Metals**, qualitative reactions, II, 551a, 565d  
 --, --, rare metals present, II, 554a, 556d  
 -- "*Metarsenobillon*," I, 492a  
**Metasomatic** change, III, 807a  
**Metastable** equilibrium, III, 447a  
**Meteorites**, III, 570d  
**Methæmoglobin**, VI, 164b, 167b  
**Methallyl** chloride fumigation, V, 397a  
**Methane**, chlorination, II, 353a, d  
 --, chlorotribromo-, II, 320d  
 --, defn., in air, II, 684a  
 --, dichlorodibromo-, II, 320d  
 --, dichlorodinitro-, I, 100d  
 --, difluorodibromo-, II, 321b  
 --, di-iodofluoro-, II, 323c  
**Methane** from carbon dioxide, II, 325d  
 -- carbon monoxide, II, 349c  
 -- phenol, II, 306d  
 --, iododifluoro-, II, 323c  
 --, nitro-, prepn., II, 373b  
 --, reaction with steam, II, 425b  
 --, tetrabromo-, II, 320b  
 --, tetrachloro-, II, 353a  
 --, tetraiodo-, II, 321c  
 --, tetranitro-, from acetylene, I, 84a  
 --, tribromo-, II, 118b  
 --, tribromofluoro-, II, 321b  
 --, trichloro-, III, 77b  
 --, trichloronitro-, III, 85b  
**Methanol**, *see also* Methyl alcohol.  
 --, defn., II, 681b  
**Methanal** of phenylglycol, I, 37a  
**Methine** bases, II, 481a, b  
**Methionine**, III, 510a  
**Methone**, IV, 5a  
**Methoxy-butaldehyde**, I, 37a  
**Methoxycatechol**, mono-, VI, 139b  
**Methoxychelidonine**, II, 527d  
**Methoxyl** group, defn., II, 621d  
**6-Methoxylepidine**, III, 178c  
**Methoxy - 5 - methylfurfural**, from mulin, II, 303b  
**Methylacetal**, I, 31c  
**N-Methylacetanilide**, IV, 416d  
**Methyl acetate**, I, 51a; II, 418b  
**Methylacetoacetic acid**, ethyl ester, I, 61b  
 -- "*Methyl acetone*," II, 471c  
 --, specification, II, 472b  
**Methylacridan - acridinium** methochloride, I, 130d  
**Methylacridinechloral**, I, 127d  
**10-Methylacridinium**, 2,8-dimino-, antiseptics, I, 133d  
**N-Methylacridone**, I, 127b  
**Methylal**, I, 34a  
**Methyl alcohol**, acetic acid from, II, 350c  
 -- carbon tetrachloride from, II, 354c  
 -- from carbon monoxide, II, 350a  
 -- in ethyl alcohol, detection, I, 184a; V, 302b  
 -- film coating, II, 149b  
 -- oxidation, II, 427c  
 -- production, II, 310d, 425c, 429c  
 -- reaction with carbon monoxide, II, 350c  
 --, specification, II, 472b  
 --, synthetic (*see also* Fischer-Tropsch synthesis), II, 425c; VI, 334a  
**Methylallene**, I, 240c  
**1-Methylamino-4-o-sulpho- $\alpha$  - tolyl - aminoanthraquinone**, I, 200d  
**Methylaniline**, I, 308b  
 -- "*Methylanol*," VI, 228a  
**2-Methylantraquinone**, I, 208b, 402b  
**4-Methylantraquinone**, 1-chloro-, I, 402c  
**Methylantraquinone**, dihydroxy-, III, 110c  
**2-Methylantraquinone**, 1:5-dinitro-, I, 391a  
 --, 1:8-dinitro-, I, 391a  
 --, 1-nitro-, I, 391a  
**Methylantraquinone**, trihydroxy-, III, 110c  
**4-Methylapigenin**, I, 12b  
**Methylapoquinidine**, III, 171a  
**Methylated spirit**, I, 182d  
 --, Industrial (Pyridinised), I, 183b; III, 557c  
 --, immaterialised, I, 183b  
 --, power, I, 183a, b  
**Methylation**, exhaustive, I, 311d  
**Methyl bromide** fire extinguisher, V, 200d  
 -- fumigation, V, 397a  
 **$\beta$ -Methylcapronic acid**, VI, 205c  
**Methylcarbinol**, acetyl-, in butter V, 300c  
**N-Methyl** carnosine in muscle, II, 392a  
**Methyl** collosolve in lacquers, II, 478d  
**Methylcellulose** in calico printing, IV, 180c  
**Methyl chloride** formation, II, 354a  
 -- chloroformate, dichloro-, III, 11b  
 --, monochloro-, prepn., III, 17a  
 --, prepn., III, 11d  
 --, trichloro-, in warfare, III, 10b  
 --, --, prepn., III, 17b  
**2-Methyl - 4 - chloro - 5 - isopropyl phenol**, II, 404c  
**Methyl** chlorosulphonate in chemical warfare, III, 10c  
 --, prepn., III, 17a  
**Methylcholanthrene** from cholic acid, II, 380a  
**Methylcinchonine**, III, 142d  
**Methylcinnamaldehyde** in cassia oil, II, 418d  
**Methyl cinnamate**, III, 181c  
**N-Methyl - d - conine**, III, 325b  
 -- *l*-conine, III, 325b  
**Methylcytisine**, II, 439b  
**Methyl** group, defn., II, 625b  
**Methyldiazo-oxide**, potassium, III, 600b  
**Methyldibromoarsine**, prepn., III, 17a  
**Methyldichloroarsine**, prepn., III, 17a  
**Methylacgonine**, benzoyl-, III, 222d  
 --, cinnamoyl-, III, 222d  
 --,  $\alpha$ -truxilloyl-, III, 222d  
 --,  $\beta$ -truxilloyl-, III, 222d  
**Methyleneaniline**, I, 308b  
**Methylenecamphor**, hydroxy-, I, 243b  
**Methylene** chloride formation, II, 354a  
 -- citric acid, III, 186b  
 -- diacetate, I, 37d  
**3:3' - Methyleneedicarbazole**, II, 279b  
**Methyl ether**, dichloro-, III, 11b  
**Methylethylacetoacetic acid**, ethyl ester, I, 64d  
**Methylethylacetonitrile**, II, 173a

- Methylethylbenzene**, III. 457a  
**as-Methylethylethylene**, I. 364d  
**Methyl ethyl ketone**, I. 71a  
 —, bromo-, in warfare, III. 10c  
 —, in film manufacture, II. 448c  
 —, specification, II. 472b  
 —, ketoxime, II. 176b  
**Methylethyl maleinimide**, I. 691b; III. 83b  
**Methyl-eugenol** in citronella oil, III. 191b  
**Methylformal**, II. 34a  
**Methyl formate** in photographic dopes, II. 448c  
**Methylfurfural**, hydroxy-, in caramel, II. 277a  
 —, —, test for, VI. 265b  
**Methylglucosides**,  $\alpha$ - and  $\beta$ -, VI. 82c  
**Methylglycocycamidine**, III. 416d  
**Methylguanidine**, VI. 140a  
**Methylguanidinooacetic acid**, III. 415a  
**1-Methylguanine**, VI. 152b  
 "Methylhexalin," VI. 220a  
**Methylcyclohexanol**, VI. 220a  
**Methylcyclohexanone** in lacquers, II. 472a  
**Methylcyclohexyl acetate** in lacquers, II. 472a  
**Methyl hexyl ketone**, II. 422a  
**Methylhydantoins**, 3- and 5-, VI. 291a  
**Methylhydrastimide** hydrochloride, I. 304c  
**5-Methyliminazole**, VI. 235d  
**3-Methylindole**, VI. 463b  
**Methyl ketopinate**, reduction II. 246b  
**Methylnaphthyl ketone**, I. 65d  
**Methyloses**, II. 287c  
**Methylo-sugars**, II. 291c  
**Methyl iso-oxazolone**, I. 63d  
 **$\gamma$ -Methyl- $\Delta^{88}$ -pentadiene**, I. 30b  
**Methyl cyclopentenophenanthrene** from cardiac agly cones, II. 382b  
 —, —, cinobufagin, II. 388a  
**Methylphenylhydrazine**, I. 293c; VI. 301c  
**Methylpropylacetic acid**, II. 271c  
**Methylisopropylacetic acid**, II. 271d  
**Methylpropylacetoacetic acid**, ethyl ester, I. 64d  
***p*-Methylisopropylbenzene**, III. 538c  
**Methyl-*n*-propylcarbinol**, I. 359b  
**Methylisopropylcarbinol**, I. 359c  
**Methylisopropylpropionic acid**, VI. 205c  
**Methylpyridines**, I. 84c  
**1-Methylquinoline**, 2- keto-1:2-dihydroxy-, III. 402c 463a  
**2-Methylquinoline**, 3-hydroxy-, I. 65c  
**Methyl salicylate**, I. 692b; II. 308d  
**Methylsalicylic acid**, V. 53a  
**Methylstibine** dihalides, I. 434d  
**Methylsulphonic acid**, monoiodo-, sodium salt, I. 4c  
 **$\alpha$ -Methylvaleric acid**, II. 271c  
 **$\gamma$ -Methylvaleric acid**, II. 271b  
**Methyl vinyl ketone**, I. 88c, 93b  
 — Violet in stability test for explosives, IV. 534a  
**Metmyoglobin**, VI. 166d  
 "Metramine," J. 320a  
**Mettegang method**, IV. 550c  
 "Mg-7," I. 253b  
**Mianin**, I. 140a  
**Micas**, I. 291c; II. 137c  
**Micelle**, III. 284a  
 — of cellulose, II. 457b  
**Michael condensation**, II. 367c  
 — with boron trifluoride catalyst, VI. 260a  
**Micranthine**, III. 547c  
**Microanalysis**, detn. of C, H and N, II. 630c  
 —, —, Cl, Br, I and S, II. 632a  
 —, quantitative, II. 629b  
**Microbalance**, McBain, III. 605b, foot-note  
**Microbalances**, I. 607c; II. 629d  
**Microcosmic salt beads**, II. 548b  
**Micro gas analysis**, II. 680d  
 — Kjeldahl nitrogen detn., II. 631c  
**Micronite**, V. 351c  
**Microspectroscope**, Zeiss, VI. 165b  
**Micro-Zeisel method**, II. 633d  
**Middle components**, IV. 195d  
**Milch den**, V. 72c  
**Milfoil**, I. 119d  
**Milk**, IV. 301b  
 —, citric acid in, III. 190b  
 — fat, see Butter.  
 — tree, II. 119a  
**Millipores**, coral from, III. 360c  
**Millet**, II. 482c  
**Millstones**, I. 4b  
**Mineral and aerated waters**, I. 155c  
**Minerals**, co-ordination formulae, III. 336a  
**Mineral waters**, detn. of metallic impurities in, I. 159b  
 "Mineral X," I. 661b  
**Minioluteic acid**, V. 52d  
**Minofor**, I. 440a  
**Minyak Nyatoh**, II. 32c  
**Miotine**, II. 200d  
 "Mischmetal," II. 516b  
**Miso**, V. 59c  
**Mispickel**, I. 469a  
**Mists**, particle size, IV. 95b  
**Mitscherlich pulp**, II. 461d  
**Mixed acid** for nitroglycerin, IV. 492d  
**M.N.T.** (mononitrotoluene), explosive, IV. 466b  
**Mocha-stone**, I. 164a  
**Mochyl alcohol**, I. 692d  
**Moddite**, IV. 519b  
**Moebius process**, VI. 108a  
**Moëllon** and moëllon dégras III. 551b, 551d, foot-note  
**Mohair**, IV. 124c  
**Mohawite**, IV. 55c  
**Mohri**, I. 123a  
**Mohua** butter, I. 653a  
**Moissanite**, II. 280c  
**Mol** concentration, III. 1d; IV. 37d, foot-note  
**Molecular depression** of freezing point, III. 441c  
 weight detn., micro-method, II. 634b  
**Mol** fraction, IV. 37d, foot-note  
**Molisch test** for chlorophyll, III. 84d  
**Mol** (molar) percentage, III. 2a; IV. 37d, footnote  
**Molybdæna**, II. 314a  
**Molybdenum carbide**, II. 281a  
 — carbonyl, II. 357a  
 — chromium alloy, III. 104d  
 detn. assay, I. 528b  
 —, colorimetric, II. 672a  
 —, electrodeposition, II. 701d  
 —, gravimetric, II. 605b  
 — in steel, I. 528b  
 —, volumetric, II. 663a  
 — with cupron, II. 605d  
 oxide cracking catalyst, II. 426b  
 — pentachloride as chlorine carrier, II. 353b  
 production, II. 511a  
 qualitative reactions, II. 554a, 556d, 575c  
 trace effect on *Azotobacter*, I. 507d  
**Monardine**, VI. 92a  
**Monascocoflavin**, V. 50  
**Monascorubin**, V. 56  
**Monazite**, II. 508c, 512b; V. 483a  
**Mond** power gas, V. 376a  
 — producer, V. 370b  
**Monel metal**, I. 278a  
**Monish** suction machine for glassware, V. 587c  
**Monite**, III. 294a  
**Monkey-nuts**, see Ground nut  
**Monobel**, IV. 553c  
**Monogermans**, V. 521d  
**Monotropin**, V. 503c  
 —, primeverose in, II. 300b  
**Monotropitin**, VI. 92a  
**Monotropitoxide**, VI. 92a  
 "Montanin" disinfectant, IV. 23a  
**Montan wax** in candles, II. 264c  
**Mont Cenis process**, I. 337b  
**Montebrasite**, I. 303d  
**Montmorillonite**, III. 190a; V. 381d  
**Moonstone**, V. 3a  
**Moore** tube in bleaching powder production, III. 62a  
**Moor-stone**, III. 32c  
**Mordant**, iron acetate, II. 53d  
**Mordants**, IV. 129d  
 —, cerium in, II. 511b  
 —, chromium in, III. 100d  
 —, detection in dyeings, IV. 173a  
 — for cotton, IV. 132a  
 —, Turkey-red oils in, II. 421d  
**Morgan gas machine**, V. 370d 371d  
**Morganite**, I. 684c, 685b  
**Morin**, I. 497d  
**Morinda** spp., VI. 92a  
**Morindin**, VI. 92a  
**Moringa** spp., I. 668c  
**Moroxite**, I. 449d

- Morphine**, diacetyl-, hydrochloride, I. 65d; VI. 205d  
**Morphium**, I. 233c  
**Morruic acid**, III. 250c  
**Mortar test**, IV. 548b  
**Mosaic gold**, I. 549d  
**Mother-of-pearl**, I. 457a  
**Moti**, II. 496a  
**Motor fuel** (*see also* Anti-knock entries; Benzene; Explosions, gaseous; Fuel; Inhibitors, gum), II. 161a  
 — fuels from hydrogenation of coal, VI. 333d  
**Mottramite**, III. 550b  
**Mou-*léou***, III. 33b  
 "Mould creams," IV. 303d  
**Mould fermentation** in food prepn., V. 59b  
 — growth on arsenical paper, poisoning due to, I. 483c  
**Moulding** of candles, II. 265c  
**Mould products** of unknown constitution, V. 56  
**Moulds**, chlorine compounds from, V. 58b  
 —, fats and lipins from, V. 57b  
 —, nitrogen compounds from, V. 58d  
 —, polysaccharides from, V. 57b  
**Mould spp.**, citric fermentations with, V. 49b  
 —, —, oxalic fermentations with, V. 49b  
 "Mould starch," V. 57d  
 "Mountain-cork," I. 499d  
 "Mountain-leather," I. 499d  
 "Mountain-wood," I. 499d  
**Movement**, Brownian, III. 280c  
**Mowrin** or mowrin, I. 651a  
**Mowha butter**, I. 653a  
 "Mowlith H" and "N," I. 90c  
**Mowrah butter**, I. 653a  
 — flowers, I. 655b  
**Mowrin**, I. 651a  
**Mucic acid**, II. 298a  
**Mucins**, VI. 21c, 20a  
**Mucor mucedo** on bread, II. 84b  
 — spp. in fermentations, *see* Fermentations, mould.  
**Müller's solution**, I. 649b  
**Mule spinning**, V. 150c  
**Mullite**, III. 197a  
**Multiflorin**, III. 556c  
**Multiple effect evaporation**, IV. 406d  
**Multiple fabrics**, V. 199b  
**Munjin**, V. 446b  
**Muntenite**, I. 302d  
**Muramontite**, II. 512b  
**Murexan**, I. 628c  
**Murexide**, I. 249b; II. 197b  
**Muriatic acid**, III. 69b  
**Murlins**, I. 199b  
**Muramontite**, II. 512a  
**Murumuru fat**, III. 88b, 244a  
**Muscarine**, III. 93d  
**Muscone**, IV. 417a  
**Muscovite**, IV. 279d  
**Musk**, II. 182a  
 —, artificial, II. 174c  
 —, Baur, II. 174c  
 —, cabardine, II. 182a  
 —, mallow, I. 304a  
**Muspratt process**, III. 67a  
**Mustard gas**, *see* Diethyl sulphide,  $\beta$ -dichloro-  
 — seed, oil of black, II. 2d
- Mutarotation** of glucose, VI. 250a  
**Mutase**, V. 429b  
**Mycoderma aceti**, III. 231d  
**Mycodextran**, V. 57d  
**Mycogalactan**, V. 58a  
**Mycophenolic acid**, V. 53c  
**Mylabris spp.**, II. 270b  
 "Myochrysin," VI. 119b  
**Myocotinine**, I. 123d  
**Myoglobin**, VI. 166d  
 — as oxygen carrier, VI. 167c  
 —, kinetics of oxygenation, VI. 167a  
**Myokynine**, I. 087b  
 "Myosalarsan," I. 102a  
**Myosin** in maize, II. 481d  
**Myrbane oil**, I. 670b  
**Myrcene** in hop oil, II. 92a  
 **$\beta$ -Myrcene**, II. 153c  
**Myricitrin**, VI. 92b  
**Myricyl alcohol** in rice, II. 493d  
 — compounds in candelilla wax, II. 262a  
**Myristic acid**, I. 199c  
 — in rice, II. 494b  
**Myristica spp.**, fats from, IV. 3d  
**Myristin** in Cay Cay fat, II. 439c  
**Myrobalans**, IV. 276d  
**Myrosin**, IV. 314b  
**Myricolorin**, IV. 391a; VI. 92b  
**Myrtillin**, VI. 92b  
**Myxoxanthin**, II. 400d  
**Myxoxanthophyll**, II. 401a
- N
- Naadsteen**, III. 573c  
**Nacrite**, III. 196a  
**Nagyagite**, VI. 102a  
**Nail-head spar**, II. 205c  
**Namara potato**, I. 497a  
**Nandimine**, IV. 55a  
**Nankin**, I. 133b  
 "Naphazole," IV. 231a  
 "Naph tazols," IV. 133a, 131a  
**Naphthacene**, III. 119c  
**Naphthacridines**, I. 120d  
**Naphthacridone**, I. 130b  
**Naphthacyanole**, III. 516c  
**Naphtha** in lacquers, II. 172a  
 "Naphthalase," I. 567d  
**Naphthalene**, antiseptic, IV. 30c  
 — bisdiazonium salts, III. 582a  
 —, carcinogenic compounds from, II. 378c  
 —, coal tar, III. 209a, 212c  
 $\alpha$ - and  $\beta$ -Naphthalene derivs., *see* I- and 2-Naphthalene.  
**Naphthalene-1-diazonium-5-sulphonate**, III. 592d  
 — 1:8-dicarboxylic acid, I. 13a  
 —, dihydroxy-, *see* Naphthalenediol.  
 —, dinitro-, for explosives, IV. 474d  
**2:3-Naphthalenediol**, antiseptic, IV. 30a  
**2:7-Naphthalenediol**, 1-nitroso-, IV. 10a  
**Naphthalene-3:6-disulphonic acid**, 1:7-dihydroxy-, I. 1a  
 —, 1:8-dihydroxy-, III. 115d  
 — from phenol, II. 306d
- Naphthalene**, hydrogenation, VI. 352c  
 — in petroleum, I. 466d  
 —, 1-methyl-7-isopropyl-, IV. 392c  
 —, mononitro-, for explosives, IV. 474c  
 —, oxidation, II. 428a; VI. 445a  
 —, 2-isopropyl-, IV. 393c  
 — recovery from coal- and coke-oven-gas, III. 265b; V. 404a  
**Naphthalenes**, nitro-, IV. 474c  
**Naphthalene**, tetranitro-, for explosives, IV. 475b  
 —, trinitro-, for explosives, IV. 475a  
**Naphthalic acid**, I. 13a  
 "Naphthanol," IV. 231a  
**Naphthaphenazine**, I. 565d, 567a  
**Naphthaquinone**, 2-hydroxy- and 5-hydroxy-, in hair dyes, VI. 171b  
 —, —, detn., VI. 171b  
**Naphthastyril**, I. 426a  
**Naphthenes**, formation, II. 173a  
 — in petroleum, III. 537b  
**Naphthindone B1**, I. 570c  
**Naphthite**, IV. 475a  
**2-Naphthol**, antiseptic, IV. 29b  
**Naphthol AS**, *see* "Naphto l AS."  
**8-Naphthol-3:6-disulphonic acid**, 1-acetamino-, I. 119d  
**2-Naphthol-3:6-disulphonic acid**, 1-amino-, sodium salt, IV. 7c  
 — in butter, test for, II. 167d  
 — candles, II. 204c  
 —, reaction with Millon's reagent, II. 307c  
**Naphthols**, 1- and 2-, hydrogenation, VI. 354b  
**2-Naphthol-8-sulphonic acid**, I. 658c; III. 428c  
**Naphthophenanthrindine**, alkaloids, II. 529b  
**1-Naphthylamine-4:6-disulphonic acid**, III. 545b  
 — 4:7-disulphonic acid, III. 545b  
**2-Naphthylamine-5-sulphonic acid**, III. 545b  
**2-Naphthylamine-6-sulphonic acid**, II. 118d  
**2-Naphthylamine-8-sulphonic acid**, I. 1a, 585d  
**2-Naphthyl benzoate**, in candles, II. 264c  
 — isobutyl ether, II. 106c  
**Naphthylene-1:8-diazoimine**, III. 593b  
 — diazoimines, 1:2- and 2:3-, III. 593b  
**2-Naphthyl ethyl ether**, II. 106b  
**2-Naphthylhydrazine**, I. 197b; VI. 301d  
**1-Naphthyl salicylate**, I. 262d  
 "Naphthol AS," IV. 133a, 134a, 227c  
**Napoleonite**, IV. 8b  
**dl-Narcotine**, VI. 100d  
 — methiodide dihydrate, VI. 100d  
**Narcyen**, I. 79b, 867d

- Naringerin**, VI. 130a  
**Naringin**, VI. 92b, 130a  
**Nasturtium officinale**, VI. 89a  
**Nasunin**, III. 554c  
**Nataloin**, I. 262c  
**Natramblygonite**, I. 303d  
**Natroalunite**, I. 298a  
**Naturgiftstoff**, III. 434c  
**Naturlab**, IV. 315c  
*"Nautisan,"* I. 70d  
**Neat's foot oil**, II. 28d, footnote; VI. 280d  
**Neb-neb**, I. 11c, 585a  
*Nectandra puchury major*, isoeugenol from, IV. 397d  
**Neem bark**, I. 561a; V. 510a  
**Neopretin**, III. 554c  
*"Nekals,"* IV. 286b  
*Nelson Bohannite,"* I. 277c  
**Nelson electrolytic cell**, III. 54c  
**Nermalite**, II. 110b  
*"Nembutal,"* (see also Barbituric acid), II. 308b, 623a  
*"Neosantimosan,"* I. 439a  
*"Neosarsphenamine,"* I. 492a  
**Neocyanine**, III. 524c  
**Neodymium**, II. 511c  
**Neocerium**, IV. 321b  
*"Neokharivan,"* I. 492a  
*"Neomerpins,"* IV. 286b  
*"Neonal,"* I. 623a  
**Neonite**, IV. 510b  
**Neopelline**, I. 122c  
*"Neosalvarsan,"* I. 480b, 492a  
*"Neostam,"* I. 430c  
**Neosterol**, IV. 325c  
*"Neostibosan,"* I. 430c  
*"Neothsin,"* I. 309a  
**Neou oil**, IV. 86d  
**Nepheline**, I. 450b, 652a  
—-fayonite, I. 450b; II. 429c  
**Nephelite**, I. 264d  
*Nephrops norvegicus*, I. 532c  
**Nepouite**, V. 430a  
**Neral**, III. 183d  
**Nerifolin**, II. 386c  
**Nerol**, II. 261b; V. 517c, 518a  
**Nerolidol**, I. 693c  
*"Nerolin Bromelia,"* and *"Nerolin Yara Yara,"* V. 328c  
*"Nerolin II,"* II. 106b  
*"Nervocidine,"* IV. 336a  
**Nervon**, II. 506c; VI. 92c  
**Nessler's reagent**, II. 572c  
**Neuberg ester**, V. 22a  
**Neurine**, III. 94a  
**Neurodin**, I. 73b  
*"Neutralisations,"* VI. 248c  
*"New Fortex,"* IV. 487b  
**Ngai-camphor**, II. 30d  
**Ng'art oil**, IV. 86c  
**Niccolite**, I. 469a  
**Nickel**, action on methane, II. 349d  
—, —, — and steam, II. 425b  
—, arsenide, III. 34d  
—, as trace element, I. 510a  
—, carbide, II. 281c  
—, carbonyl, II. 351a, 357a  
—, chromium alloy, III. 104b  
—, complexes with catechol, II. 431a  
—, detn. assay, I. 528c  
—, —, colorimetric, II. 672b  
—, —, electrodeposition method, II. 701d  
—, —, gravimetric, II. 612c; V. 402c  
**Nickel**, detn., volumetric, II. 603b  
—, drop reaction, II. 581a  
—, electrodeposition, IV. 265c  
—, glance, I. 469a  
—, in oxidation of sulphur compounds, II. 425a  
—, phosphide, formation, II. 357d  
—, qualitative reactions, II. 553a, 578a  
—, —, rare metals present, II. 555d, 556d  
—, silver, II. 105d  
—, sulpharsenide, V. 529c  
—, uranyl acetate test for sodium, II. 554c  
**Nicol's prism**, substitute, II. 443a  
**Nicotine**, antiseptic, IV. 31b  
*Nigella spp.*, III. 545d  
**Nigrosine**, I. 509b, 579c; VI. 467d  
**Nikeline**, I. 409a  
**Ninhydrin**, I. 324b; VI. 307c, 308a  
**Niobates**, qualitative reactions, II. 555d, 556d, 573d  
**Niobic acid**, III. 312a  
**Niobite**, III. 309c, 310b  
**Niobium** (columbium), III. 309d  
—, and tantalum, separation, II. 602a  
—, arsenide, III. 313b  
—, boride, III. 313b  
—, bromide, chloro-, III. 312d  
—, carbide, II. 218d; III. 313b  
—, chloride, chloro-, III. 312d  
—, detn., gravimetric, II. 602a  
—, dioxide, III. 312a  
—, hydroxide, chloro-, III. 312d  
—, monoxide, III. 311d  
—, nitride, III. 313a  
—, oxybromide, III. 313a  
—, oxychloride, III. 313a  
—, oxyfluoride, III. 312c  
—, oxysulphide, III. 313c  
—, pentabromide, III. 313a  
—, pentachloride, III. 312c  
—, pentafluoride, III. 312c  
—, pentoxide, III. 312a  
—, phosphide, III. 313b  
—, prepn. from its oxide, II. 511a  
—, qualitative reactions, II. 555d, 558b, 573d  
—, sesquioxide, III. 312a  
—, sulphide, III. 313b  
—, trichloride, III. 312c  
*"Nipagin,"* VI. 340b  
**Niquidine**, III. 149d, 171a  
**Niquine**, III. 149d, 170a  
*isoNiquine*, III. 170b  
*"Nirvanine,"* I. 369b  
**Nisinic acid**, III. 247b  
**Nitramide**, catalytic decomposition, VI. 249c, 255b  
**Nitrate**, detn., colorimetric, II. 673c  
—, —, gravimetric, II. 598c; V. 327d  
—, —, Schlösing gasometric, II. 688d  
—, —, volumetric, II. 604a; IV. 515b  
—, of soda fertiliser, V. 65b  
**Nitrates and nitrites**, detn., II. 687d, 688d; IV. 515a; V. 290b; VI. 150b  
**Nitrates**, detection and detn., V. 327d  
—, drop reaction, II. 582a  
—, qualitative reactions, II. 572c  
**Nitrator-separator** for nitroglycerin, IV. 494c  
**Nitric acid**, catalytic production, II. 424b  
—, —, detn., see Nitrates.  
—, —, for nitroglycerin, IV. 492c  
—, —, solvent in analysis, II. 549b  
—, —, use in flour analysis, II. 83a  
—, ester explosives, IV. 480c  
—, ether, IV. 364d  
—, oxide, detn., II. 684b  
**Nitriles**, II. 371d, 377b  
—, hydrolysis, II. 362d  
—, unsaturated, preparation, II. 385b  
*isoNitriles*, I. 309a  
**Nitrite**, detn. (see also Nitrate, detn.).  
—, —, potentiometric method, II. 707d  
—, —, volumetric, II. 604c  
**Nitrites**, qualitative reactions, II. 572d  
**Nitro-amino explosives**, IV. 485a  
**Nitrocellulose**, analysis by nitrometer, II. 687d; IV. 515a  
—, dopes (see also Celluloid; Cellulose lacquers; Cellulose plastics; Fibres, artificial, or rayon), II. 464b  
—, explosives, IV. 501-535  
—, gelatinisation, II. 252c, 259d  
—, history, IV. 501c; V. 114d  
—, in celluloid, II. 443b  
—, —, photographic films, II. 447a  
—, lacquers, II. 467d  
—, nitroglycerin powders, IV. 519a  
—, plastics, II. 474b  
—, powders, IV. 517c, 524d  
—, —, cutting and pressing process, IV. 525d  
—, —, drying, IV. 526b  
—, —, progressive burning, IV. 527a  
—, —, solvents for gelatinising, IV. 523c  
—, —, treatment of deteriorated, IV. 527a  
—, —, production, II. 448c, 447a, 463d; IV. 502c  
—, silk, see Rayon.  
—, soluble, see Collodion cotton.  
—, stabilisers, IV. 520a  
—, stability tests, see Stability tests.  
—, theory of nitration, IV. 502d  
**Nitrochalk**, I. 352d; V. 65c  
**Nitro-compounds**, detn., with titanium chloride, II. 627a, 708a  
**Nitrocotton**, see Nitrocellulose.  
**Nitro-explosives**, classes, IV. 465a, 475c, 484c, 485a, 489d, 501c, 517c  
—, stability tests, see Stability tests.  
**Nitroform** from acetylene, I. 84a

- Nitrogen**, detn. by hydrogenation, VI. 362*d*  
 —, —, gasometric, II. 684*b*  
 —, —, in Ca cyanamide, V. 84*c*  
 —, —, carbon compounds, II. 617*d*, 631*b*  
 —, —, feeding stuffs, IV. 601*d*  
 —, —, fertilisers, II. 619*b*; V. 83*d*  
 —, —, hydrogenation analysis, VI. 362*d*  
 —, —, nitrates, II. 661*a*; V. 84*d*  
 —, —, Kjeldahl's method, II. 619*b*; IV. 602*a*; V. 81*b*  
 —, —, micro-Dumas method, II. 631*b*  
 —, —, —Kjeldahl method, II. 631*c*  
 —, —, dioxide, detn., II. 684*c*  
 —, —, free extract, IV. 599*d*  
 —, —, luminescent, III. 23*c*  
 —, —, pentoxide, decomposition, II. 531*c*  
 —, —, peroxide in flour bleaching, II. 81*b*  
 —, —, reaction with calcium phosphate, II. 225*b*  
 —, —, —lime, II. 222*d*  
 —, —, production and purification, I. 335*a*  
 —, —, trichloride in flour bleaching, II. 81*a*
- Nitroglycerin** (see also *Blasting gelatine*; *Dynamite*), IV. 191*c*, 196*d*  
 —, continuous manufacture, IV. 496*b*  
 —, detection, IV. 199*c*  
 —, detn., IV. 532*d*  
 —, effect of cooling or heating, IV. 497*a*, *c*  
 —, explosive properties, IV. 498*c*  
 —, manufacture, IV. 491*d*  
 —, recovery of acids, IV. 495*d*  
 —, treatment of waste wash water, IV. 495*c*  
 —, physiological effects, IV. 498*b*  
 —, properties, IV. 496*d*  
 —, recovery, from waste acids, IV. 495*d*  
 —, solubility, IV. 497*d*  
 —, stability, IV. 497*b*  
 —, testing, IV. 499*d*  
 —, volatility, IV. 496*d*
- Nitroglycol**, IV. 489*d*
- Nitro-groups**, detn., II. 627*a*  
 —, "*Nitrolim*," II. 219*c*; V. 65*d*
- Nitrolit**, IV. 484*a*
- Nitromannitol**, IV. 500*d*
- Nitrometer**, I. 582*c*  
 —, Lunge's, II. 687*d*  
 —, "*Nitron*," VI. 150*a*
- Nitroprusside**, sodium, III. 477*a*
- Nitroprussides**, qualitative reactions, II. 569*c*  
 —, "*Nitrosamines*" for diazo coupling, IV. 231*c*
- Nitro-silk** (see also *Nitrocellulose*), II. 464*b*; V. 114*d*
- Nitrosocarbonyls**, II. 358*b*
- Nitroso R-salt**, reagent for cobalt, II. 552*d*
- Nitrostarch**, IV. 516*d*
- Nitro-sulphur compounds** as explosives, IV. 484*c*
- Nitrous fumes**, analysis, II. 684*b*  
 —, oxide, detn., II. 684*c*
- Nitrum seri lactis**, II. 290*a*
- Njatua** tallow, II. 32*c*
- Nobelit**, IV. 556*a*
- Nobel's blasting oil**, IV. 191*d*  
 —, "*Noctal*," I. 623*a*
- Nodakenin**, VI. 92*c*
- Nogueira de Iguaque**, II. 262*c*
- Nohlite**, II. 512*c*
- Nomograms**, III. 3*c*, 5*a*
- n-Nonacosane**, occurrence, II. 119*c*, 183*a*
- 15 - Nonacosanol**, 15 - non-acosanolone, occurrence, II. 119*c*
- Non-metals**, drop reactions, II. 581*d*
- Nontronite**, I. 663*b*; III. 196*a*
- Nopal**, *Nopalca coccinellifera*, III. 226*c*
- Nopaleries**, III. 226*c*
- Norbixin** from lycopene, II. 101*b*
- Norcamphor**, methylation of, II. 210*b*
- Norcantharidin**, II. 270*d*
- Norcaryophyllic acid**, II. 409*b*
- Norcassaidine**, IV. 330*a*
- Norconessine**, III. 323*c*
- Norisoeophrine**, II. 430*b*
- $\delta$ -Norisoeophrine** (anthine), I. 11*b*
- $\alpha$ -Norequilenin**, VI. 271*c*
- Norsupitton**, IV. 401*c*
- Norharman**, VI. 186*a*
- Nor-m-hemipinic acid**, II. 238*a*  
 —, "*Norit*," I. 153*a*; II. 316*d*
- Norite**, III. 327*c*
- Norsabite**, IV. 556*d*
- "Norwegian gabbro"**, V. 109*a*
- "Nosophen"**, I. 418*d*
- Noumeite**, V. 429*d*
- Noumgou** fat, I. 655*a*
- Novaine**, II. 391*a*  
 —, "*Novarsenobenzene*," I. 192*a*  
 —, "*Novarsenobillon*," I. 492*a*
- Novit**, IV. 489*c*  
 —, "*Novocaine*," I. 1*b*, 369*a*; II. 316*b*
- Nuocite**, VI. 495*a*
- Nuclease**, IV. 314*b*
- Nucleation** in supersaturated solutions, III. 416*d*
- Nucleic acid**, oryza-, II. 409*a*  
 —, acids, VI., 92*c*
- Nuclei** in condensation of vapours, IV. 97*c*, 98*b*
- Nuclein** in rice, II. 409*a*
- Nucleotides**, II. 287*b*
- Nullipores**, coral from, III. 360*c*  
 —, "*Numal*," I. 623*a*  
 —, "*Nupercaine*," I. 309*c*  
 —, "*Nupyrin*," I. 517*d*
- Nut butters**, II. 168*d*
- Nutmeg** butter, II. 168*d*
- Nut oil**, III. 33*a*
- Nutritive** ratio, IV. 601*b*
- Nuts**, oil, aoura, III. 238*b*  
 —, —, babassu, III. 213*d*  
 —, —, burity, III. 238*b*  
 —, —, cohune, III. 213*d*  
 —, —, gru-gru, III. 238*b*  
 —, —, maja, III. 238*b*  
 —, —, jauary, III. 238*b*  
 —, —, kokerite, III. 238*b*  
 —, —, mocaya, III. 238*b*  
 —, —, murity, III. 238*b*
- Nuts**, oil, murumuru, III. 244*a*  
 —, —, palm-kernel, III. 243*a*  
 —, —, Paraguay, III. 238*b*  
 —, —, piririma, III. 238*b*  
 —, —, tucum, III. 238*b*
- Nyctanthin**, II. 439*d*
- Nylon**, IV. 125*d*, 120*a*; V. 112*b*, 113*b*, 120*a*

## O

- O-Acid**, VI. 152*d*
- Oak-apples**, V. 126*b*
- Oakley** quarry powder, IV. 487*b*
- Oats**, II. 480*b*
- Obermuller** test, IV. 547*d*
- Oblitine**, II. 391*b*
- Océmene**, II. 155*d*
- Ochroite**, II. 512*b*
- Ocimene**, II. 153*c*
- Ocimum** spp., eugenol from, I. 652*c*; IV. 391*c*
- $\Delta^8\alpha$ -Octadiene**, II. 156*d*
- Octaethylene glycol**, IV. 370*b*
- Octahedrite**, I. 370*a*
- Octahydroeugenol**, IV. 396*c*
- isoOctane** aviation fuel, VI. 333*d*
- cycloOctatetraene**, III. 535*b*
- $\alpha\gamma$ -Octatrien- $\gamma$ -ine**, I. 88*b*
- Octylacetoacetic acid**, ethyl ester, I. 61*c*  
 —, sec.-Octyl alcohol, prepn., II. 422*a*
- Octyl** butyrate, occurrence, II. 179*c*
- Octylformal**, I. 31*b*
- sec.-Octylhydrocupresine**, III. 108*b*
- Odorin**, II. 29*d*
- Odibutumen**, V. 354*a*
- Enanthaldehyde** in cognac oil, II. 122*a*
- Enanthol**, VI. 205*a*
- Enanthylic acid**, VI. 205*a*
- Enin**, III. 554*c*; VI. 92*c*
- Estradiol**, VI. 269*a*
- $\alpha$ -Estradiol**, VI. 269*c*
- $\beta$ -Estradiol**, VI. 269*c*
- Estriol**, VI. 268*c*, 269*a*, *c*  
 —, glycuronide, VI. 269*b*
- Eestrogens**, artificial, VI. 272*a*  
 —, colour reactions, VI. 269*d*  
 —, origin, VI. 270*d*  
 —, synthesis, VI. 271*a*
- Estrone**, VI. 268*c*, *d*  
 —, properties, VI. 269*b*
- Oil**, animal, II. 29*d*  
 —, "*Oil*, atomised," V. 370*c*
- Oil**, boiled or kettle-boiled, I. 26*b*; IV. 91*a*
- Oilcakes**, fertiliser, V. 66*b*
- Oilcloth**, American, V. 195*a*  
 —, manufacture, V. 195*a*  
 —, "*Oildag*," I. 119*d*; II. 310*b*; III. 288*a*
- Oiled silk**, V. 195*d*
- Oil emulsions**, edible, IV. 303*b*
- Hydrosols**, IV. 284*a*  
 —, in feeding stuffs, IV. 592*d*, 601*d*  
 —, point, V. 351*d*  
 —, process in photography, III. 111*a*  
 —, pulp, I. 293*c*  
 —, refining, see *Earths*, active.

- Oils**, boiled, "bung-hole," II. 266; IV. 91b  
 —, decolorizing, IV. 247c, 240b  
 —, desulphurisation, II. 426b  
 —, drying, IV. 81c  
 —, —, non-drying and semi-drying, IV. 81d  
 —, —, refined, for paints, IV. 87c  
 —, —, synthetic, I. 90b; II. 422b; IV. 81d, 87b  
 —, effect on concrete, II. 118b  
 —, hardened or hydrogenated (see also Hydrogenation), II. 426d; VI. 177b  
 — in casein paints, II. 415c  
**Oleikins**, V. 195d  
**Oils**, sulphurised (see also Factic), IV. 90c, 500a  
**Olestones**, I. 4c  
**Oleotica** oil, IV. 84a  
**Olenite**, I. 227c  
**Olanin**, II. 29d  
**Oleandrogenin**, II. 380c  
**Oleandrin**, II. 380b; VI. 92c  
**Oleandrose**, II. 380c  
**Oleianolic** acid as aglucone in calendula saponin, II. 231b  
**Oleates**, metallic, parasiticide, IV. 28c  
**Olefiant** gas (ethylene), I. 79c; IV. 372b  
**Olefin** oxides, glycol ethers from, II. 443a  
**Olefins**, alkylation of carbazole with, II. 280a  
 — from carbon monoxide, II. 350d  
 — — shale oil, II. 3b  
 —, oxidation, II. 373a  
 —, poly-, II. 151a; III. 533c  
**Oleic** acid, III. 247b  
 —, antiseptic action, IV. 28b  
 —, glycerides (see also Drying oils; Olein), VI. 68b  
 — in bone fat, II. 29b  
**isoOleic** acid, detn., VI. 185b  
 —, formation, VI. 184c  
 —, in candles, II. 264a  
**Olein**, enzymatic synthesis, II. 420c  
 — in Cáy Cáy fat, II. 439c  
**Ol. Elliotti**, III. 435b  
**Oleum anethi**, I. 371c  
 — *animale empyreumaticum*, II. 29d  
 — *calcis*, II. 213a  
 — *Dippelii*, II. 29d  
**Oleyl** alcohol in wool scouring baths, II. 10a  
**Olibanum** (see also Frankincense), II. 53c; V. 328d  
**Oligoclase**, V. 1d  
**Oligodynamic** action, IV. 24d  
**Oligosaccharides**, II. 301b  
 —, optical rotation, II. 302b  
**Olive**, Caledon, R. I. 422c; II. 119b  
 —, Cibanone, B. I. 424a  
 — oil in wool scouring baths, II. 16a  
**Olivine**, I. 500b; III. 119d  
 — basalt, I. 652a  
**Onegite**, VI. 101a  
**O'Neill** glass-blowing machine, V. 583  
 — suction machine for glass-ware, V. 680  
**Ononin**, V. 259c; VI. 92a  
**Oxyz**, I. 164a  
**Oöspora** spp., V. 57a  
**Oosporin**, V. 58  
**Opacifiers** in candles, II. 264c  
**"Ophorite"**, IV. 464d  
**Optochin**, III. 166b, 168b  
**Orange**, Acid, IV. 205a  
 —, Acridine, and Orange Acridine R, I. 131d, 132c  
 Algal, I. 206a  
 Alizarin, I. 205a, 206a, 228a  
 — G, J. 228b, 393a  
 Cadmium, II. 194d  
 Caledon Gold, 3G, I. 422c  
 —, 4R, RRT, I. 419a  
 — Chrome, III. 112b, 113a  
 —, Cibanone, R, 6R, I. 423c, 417a  
 "Orange crystals," I. 65d  
**Orange**, Indanthrene, F3R, RRK and 6RTK, I. 418a, 416d, 414c, 420a  
 —, Brilliant, GK, GR and RK, I. 426a, 427d, 420c, 426a  
 —, — Golden, GN, I. 396c, 418d  
 Ionamine, CB, I. 40c  
 New Acridine, R, I. 132a  
 Pharma Acridine, R, RRR, I. 132a  
 pigments from the, III. 184d  
 Rhodulin, N, NO, I. 132a  
 Soledon Brilliant, 4R, I. 429b  
**Orbitolites marginalis**, coral from, III. 300b  
**Or bleu**, VI. 110a  
**"Orcas,"** I. 136d  
**Orcinol**, colour reaction with pentoses, II. 287b  
**Ores**, flotation process, V. 263d  
**Organic** finishing, V. 191a  
**Organophosphors**, II. 221a  
**Organosols**, III. 270d  
**Organzine** silk, IV. 124a; V. 94a  
**Or gris**, VI. 110a  
**Orixine**, III. 602d  
**Orizabin**, VI. 90c  
**Ornithine** from citrulline, III. 103b  
**Ornithine**, II. 224c  
**Orobanchin**, VI. 92d  
**Oroboside**, VI. 92d  
**"Orphol,"** I. 701a  
**Orpiment**, I. 468c, 479b  
**Orsat** apparatus, II. 676a  
**Orthite**, I. 238c; II. 512a, b  
**Orthoboric** acid, II. 46d  
**Orthochrome T**, III. 515b  
**Orthoclase**, I. 264d  
**"Orthoform"** (new and old), I. 369b  
**"Ortizon,"** VI. 345d  
**Orujo**, II. 343b  
**Oryzanin**, II. 60d  
 — in rice, II. 492b  
**Osmium**, detn., II. 613a  
 —, —, gravimetric, II. 613b  
 —, —, volumetric, II. 604d  
 —, qualitative reactions, II. 554d, 556d, 578d  
**Osmotic** pressure, equation for, III. 288a  
 — of starch solutions, II. 302b  
**Osones**, II. 293c  
**Ossein**, II. 27a; V. 505b; VI. 23a, 25a  
**Osteolite**, II. 224c  
**Ostwald** dilution law, II. 536c  
**Osyritrin**, VI. 92d, 95a  
**Otavite**, VI. 136d  
**Otto** of roses, I. 547b  
**Oubain**, II. 380a; VI. 92d  
**Oubagenin**, II. 380c  
**Ouredé** fat, I. 655a  
**Ovalbumin**, prepn., IV. 254b  
**Ovomucin**, prepn., IV. 254d  
**Ovomucoid**, IV. 254d  
**Oxacarboxyanines**, oxa-2'- and oxa-4'-cyanines, III. 520b  
**Oxalates**, qualitative reactions, II. 569d  
**Oxalic** acid, activated, VI. 261b  
 — from cellulose, II. 467d  
 — in carambola, II. 276a  
**Oxaly** chloride, reaction with tetralin, II. 364a  
**Oxanthrones**, I. 215a, 388b, 430d  
**Oxazine**, I. 565a  
**isoOxazolediazonium** salts, III. 592b  
**Oxazolo-cyanines**, III. 521d  
**Oxidase** in rice, II. 495d  
**Oxidases**, IV. 315b  
**Oxidation-reduction** analysis, II. 706c  
 — — potentials, VI. 417c  
**Oxide** films on metals, III. 308b  
 — scale on hot metals, III. 369a  
**Oxidoethylene** -  $\alpha\beta$  - dicarboxylic acid, V. 51d  
**Oximes**, prepn., VI. 403a  
**Oximinoethylquinuclidine**, III. 164c  
**Oximinovinylquinuclidine**, III. 159b  
**Oxindole**, VI. 464d  
**Oxine**, II. 583b; III. 335b  
 —, reagent (see also Quinoline, 8-hydroxy-), II. 583b; III. 335b  
 —, metallic compounds, II. 583b; III. 335b  
**Oxland** and Hocking's calciner, I. 473d  
**Oxonitine**, I. 121d  
**Oxonium** ion, VI. 247c  
**Oxo-reaction** of chlorophyll, III. 84c  
**Oxyacanthine**, I. 682d, 683c; VI. 496c  
**Oxy-acetylene** cutting, I. 115c  
**2-Oxy-6-aminodihydro-pyrimidine**, III. 545c  
**Oxyapatite**, II. 225c  
**Oxy- $\alpha$ -carotene**, II. 399b  
**Oxycellulose**, II. 302a  
**Oxychelidonine**, II. 527d  
**Oxycoccicyanin**, VI. 92d  
**Oxycoccin**, III. 414d  
**Oxydases**, II. 60d; IV. 315b  
**Oxygen**, detn., colorimetric, II. 685d  
 —, —, gasometric, II. 678a, 684d  
 —, —, hydrogenation analysis, II. 622b; VI. 359c  
 —, free, detection, II. 574a, 678a, 681a, 685a  
 —, qualitative reactions, II. 574a  
**Oxyhaemoglobin**, VI. 104d, 165c, 166a  
 —, detn., VI. 166c  
 —, oxygen capacity, VI. 166c  
 —, physiology, II. 21b  
**"Oxylene"** fireproofing, V. 216d



"*Oxylquit*," IV. 546a  
*N-Oxymethyl* carbazole, II. 279b  
*Oxymuriatic* acid, III. 36c  
*Oxyneurine*, I. 686a  
*6-Oxypurine*, VI. 408b  
"*Ozalide*" photographic paper, III. 589d  
*Ozokerite*, II. 500d  
— in candles, II. 264c  
*Ozone*, detection, II. 574a, 685a  
—, detn., II. 685a  
*Ozonides*, of olefins, II. 152c

P

*Pachwai*, I. 580a  
*Pack* machines in dyeing, IV. 130a  
*Paddy* or *Padi*, II. 489d  
*Padi lengkawang*, II. 31d  
*Paeonia* *off.*, *P. albiflora*, VI. 92d; I. 511d  
*Paeonin*, VI. 92d  
*Paeonol*, I. 618c  
*Pagodite*, I. 162c  
*Paint*, *see also* Cellulose lacquers; China wood oil; Driers; Drying oils; Laid-seed oil; Pigments.  
—, casein in, II. 114b  
—, emulsions, IV. 303a  
*Paints*, candlenut oil in, II. 263a  
—, carbon in, II. 313a  
—, fish oils in, IV. 85b  
— for protecting metals, III. 393b  
*Palaequium* fat, II. 32c  
— nut oils, II. 32a  
*Palás-képlű*, II. 157d  
*Palembang* benzoin, I. 615b  
*Palitantin*, V. 53a  
*Palladium*, detn., electro-deposition, II. 702a  
—, —, gravimetric, II. 614b  
—, —, volumetric, II. 665a  
—, electrodeposition, IV. 270a  
— hydride, VI. 305c, 315a  
—, qualitative reactions, II. 554d, 556d, 578d  
*Palladium* salts, reduction by carbon monoxide, II. 251b  
*Palmarosa* oil, V. 517a  
*Palmatine*, I. 124a; II. 235b  
—, tetrahydro-, III. 402a  
*Palmatisine*, I. 124a  
*Palmiacol*, II. 516d  
*Palmine*, III. 242a  
*Palmitate*, I. 549b  
*Palmitic* acid in bone fat, II. 29b  
— — — candles, II. 263c  
— — — cascarrilla and celery oils, II. 441a, 441d  
— — — rice, II. 494b  
*Palmitone* in cabbage, II. 182d  
*Palm* kernel oil, III. 243a  
— — olein, III. 243c  
— — stearin, III. 243b  
— oil in candles, II. 263d  
— — chocolate, III. 88c  
— seed oils, *Palme* *spp.*, III. 238a  
— wine, I. 487d  
*Palygorskite* group, I. 499c  
*Panabase*, IV. 590c  
*Pancolastites*, IV. 545d

*Pandermitte*, II. 55b, 40d, 48c; III. 278c  
—, borax manufacture from, II. 46d  
*Panicol*, II. 485b  
*Paniculatine*, I. 124a  
*Pantal*, I. 253b, 277c  
"*Panthesine*," I. 369a  
"*Pantocaine*," I. 369a  
*Pantothenic* acid, II. 98c; VI. 138d  
*Papain*, IV. 315a  
— protease, II. 88a  
*Papaver somniferum*, *P. spp.*, I. 450d; IV. 85d; V. 91d, 263c  
— *spp.*, anthocyanins in, I. 381d  
*Papayotin*, III. 568a  
*Paper* dryer, IV. 72a  
— manufacture, casein in, II. 414b  
— mulberry, II. 119a  
— rice, II. 490d  
— spar, II. 203c  
*Papilionaceæ*, alkaloids, III. 542c  
*Paprika*, II. 273b  
— assay, piperine standard, II. 275a  
*Parabanic* acid, I. 214d  
*Parabutaldehyde*, II. 157a  
*Paraisobutaldehyde*, II. 157b  
*Paracasein*, II. 525d  
*Parachloralose*, III. 35d  
*Parafactis*, IV. 590a  
*Paraffin* in cacao butter, II. 187a  
*Paraffins* from shale oil, II. 3b  
—, higher, detn., II. 684b  
*Paraffin* wax emulsions, V. 197a  
— in candles, II. 263c  
*Paraformaldehyde*, V. 318d  
*Paraglyoxal*, VI. 98c  
*Parahæmatin*, VI. 164b, d  
*Parahilgardite*, VI. 230c  
*Parahopeite*, VI. 206a  
*Paraldehyde*, I. 21b, 25c, 195d, 368b  
—, reaction, with caramel, II. 277a  
*Paraldol*, I. 26b, 161a  
*Paralinolic* acid in chaulmoogra oil, II. 522d  
*Paranaphthalene*, I. 382a  
*Paranephrin*, I. 147d  
*Paranthracene* (dianthracene) I. 384d  
*Parchmentising* in cotton finishing, V. 191a  
*Parchuolite*, I. 264c  
*Paricine*, III. 128a, 168c  
*Parigenin* (sarsapogenin), VI. 95c  
*Parillin*, VI. 95c  
*Parinaric* acid, IV. 86d  
*Parisite*, IV. 279a  
*Parison*, V. 578d  
"*Parkerising*" metals, III. 392d  
*Parkesine*, II. 443b  
*Particles*, liquid, vapour pressure, IV. 97c  
*Pasque* flower, I. 371b  
*Paste* (gem), V. 513b  
*Pasteur* effect, I. 557c; VI. 80c  
—, inhibition, VI. 81a  
*Pasteurisation* of beer, II. 102d  
*Pasteur* reaction of cinchona alkaloids, III. 156c  
*Patent* stills, I. 178b  
*Patina*, III. 336b, 351b, 360d, 373a, 392a  
—, artificial, III. 336b, 392c  
—, protective, III. 392a  
*Patronite*, V. 60a  
*Pauli* exclusion principle, I. 545a  
*Paullitanic* acid, VI. 153d  
*Pavy's* solution, I. 640a  
*Payta* bark, III. 128b  
*Paytamine*, III. 128b  
*Paytine*, III. 128b  
"*P.C. fibre*," V. 126b  
*Peach* wood, II. 68a  
*Pea-nuts*, *see* Ground-nut.  
*Pearl-spar*, IV. 53c  
*Peat*, V. 337b  
—, gasified, V. 338a  
*Pebble* powder, IV. 458d  
*Péchiney* process, III. 67a  
*Pectase*, IV. 314b  
*Pectenine*, II. 390c  
*Pectenoxanthin*, II. 401d  
*Pectic* acid from flax, V. 162a  
*Pectinase*, IV. 314b  
*Pectin* from pectocellulose, II. 407b  
— — pomace, III. 127d  
— in gentian root, V. 515d  
— of grape fruit peel, VI. 130b  
—, uronic acid in, II. 298a  
*Pectocellulose*, II. 407a  
*Pedersen* process, I. 268b  
*Peeling* (pottery), VI. 12b  
*Peganum harmala*, alkaloids, VI. 186a  
*Pegmatite*, VI. 126b  
*Peimine*, V. 330b  
*Peiminine*, V. 330b  
*Pei Mu*, V. 330a  
*Pelargonidin*, I. 381c; II. 234c; VI. 93a  
*Pelargonin*, VI. 93a  
*Pelargonium* *spp.*, V. 519a; VI. 88c  
*Pelosine*, I. 660c  
*Penang* benzoin, I. 615b  
— isinglass, II. 102a  
*Pencil-ore*, VI. 160d  
*Pencils*, copying-ink or indelible, III. 359d  
*Pencil-stone*, I. 162c  
*Penicillic* acid from *Penicillium* *spp.*, V. 52d  
*Penicilliopein*, V. 55c  
*Penicillium* *spp.* (*see also* Fermentation, mould), II. 84b; VI. 91c  
— — and arsenic compounds, I. 483d  
*Penrhyn* powder, anti-frost, IV. 556b  
*Pentaborane*, II. 40d  
*Pentacarbocyanines*, III. 528a  
*Pentacyanides*, III. 476b  
*cycloPentadecanone*, IV. 417a  
*cycloPentadiene*, III. 534b  
— from phenol, II. 806d  
*Pentaerythritol*, IV. 499d  
— tetranitrate, IV. 499d, 500d  
*Pentaethylene glycol*, IV. 379b  
*Pentamethylene diamine*, II. 188c  
— tetrazole, II. 388c  
*Pentamethylglucose*, II. 291d

- Pentane**, amyl deriva. from, II. 471*d*  
**isoPentane**, chlorination, II. 154*d*  
 —, dichloro-, II. 154*d*  
 "**Pentanol**," I. 361*a*  
**Pentaxanthin**, II. 401*d*  
 "**Pental**," I. 623*a*  
**Penthrut**, IV. 490*d*  
**Pentitol**, VI. 495*d*  
 "**Pentobarbital**," I. 623*a*  
**Pentosan**, bran, II. 56*a*  
 — in cabbage, II. 183*b*  
**Pentosane**, II. 287*a*, 303*c*  
 — in celery, II. 441*b*  
 — cellulose material, II. 402*c*  
**Pentyl**, IV. 488*b*  
**Pepper**, red, II. 273*b*  
**Pepsin**, IV. 311*d*, 315*a*  
**Peptides**, synthesis, I. 322*a*  
**Peptisation**, III. 281*a*  
**Peracetic acid**, I. 24*a*, 50*a*; II. 373*a*  
**Peracids**, detn., volumetric, II. 665*a*  
 —, oxidation of aldehydes by, II. 302*b*  
 —, prepn., II. 373*a*; VI. 345*b*  
**Perammon**, IV. 464*d*  
**Perbenzoic acid**, II. 373*a*  
**Perborate** bleaching of silk, II. 18*c*  
 —, detn., volumetric, II. 665*a*  
**Perborates**, II. 51*c*; VI. 315*c*  
 —, qualitative reactions, II. 568*a*  
**Perborax**, II. 51*d*; VI. 345*c*  
 "**Percaline**," I. 369*c*  
**Percarbonate**, detn., volumetric, II. 665*a*  
**Perchlorate**, detn., volumetric, II. 657*b*  
 — explosives, IV. 461*c*  
**Perchlorates**, detn., gravimetric, II. 610*a*  
 —, production, III. 68*b*  
 —, qualitative reactions, II. 576*d*  
**Perchloric acid** in analysis, precautions necessary, II. 557*d*, 563*d*  
**Perchloroethyl formate**, IV. 382*a*  
 "**Perchloron**," III. 63*b*  
**Perchromic acid**, III. 114*a*  
**Per-compounds**, II. 373*a*; VI. 345*b*  
**Percussion caps**, IV. 543*c*  
 —, sensitiveness of explosives to, IV. 551*a*  
**Perdisulphate** (persulphate), detn., volumetric, II. 665*a*  
**Pexarine**, V. 504*a*  
**Pereiro bark**, V. 503*d*  
**Perfect gas**, definition, VI. 412*a*, 413*d*  
**Perfumery**, use of butyric esters in, II. 181*b*  
 "**Perhydrite**," VI. 345*d*  
**Pericol**, III. 515*b*  
**Perilla oil**, IV. 84*b*  
**Perilla spp.**, IV. 84*b*  
**Periodates**, detn., gravimetric, II. 610*d*  
 —, volumetric, II. 657*b*  
 —, qualitative reactions, II. 577*b*  
**Periplocin**, II. 386*d*; VI. 93*a*  
**Periplocymarin**, II. 386*a*; VI. 93*a*  
**Periplogenin**, II. 382*a*, 386*d*  
 "**Peristaltin-Ciba**," II. 410*d*  
**Peristerite**, V. 3*a*  
**Perkin reaction**, II. 364*c*; III. 180*d*  
**Pernanganate**, detn., potentiometric, II. 708*b*  
 — in respirators, III. 10*c*  
 — volumetric analysis, II. 646*c*, 660*b*, 602*a*  
**Pernanganates**, qualitative reactions, II. 577*c*  
**Permitted explosives**, IV. 553*c*, 558*b*, 558*b*  
 —, sheathed, IV. 556*d*, 561*d*  
**Pernonosulphuric acid**, VI. 341*a*  
 "**Permutite**," II. 220*b*; VI. 276*d*  
**Pernambuco wood**, II. 68*a*  
**Perniobic acid**, III. 312*b*  
 "**Pernocton**," I. 368*b*, 623*a*  
**Pervovskite**, II. 229*d*; IV. 245*a*  
**Peroxidase**, IV. 315*b*; VI. 168*a*  
 —, compound with hydrogen peroxide, VI. 168*a*  
 —, detection, V. 304*c*; VI. 142*b*  
 — in rice, II. 495*d*  
**Peroxide** bleaching of cotton, silk, wool, II. 10*c*, 18*c*, 17*a*; V. 204*a*  
 — rayon, V. 204*a*  
 —, detn., volumetric, II. 661*d*  
**Peroxides**, acyl, prepn., II. 373*a*  
 "**Peroxydol**," VI. 345*c*  
**Perpluviation** extraction, IV. 584*d*, 585*c*  
**Perry**, J. 166*b*; III. 120*c*  
**Perseitol**, II. 296*d*  
**Perseulose**, II. 286*d*  
**Persulphate**, detn., volumetric, II. 665*a*  
 — in flour, II. 81*a*  
 — production, VI. 311*c*  
**Persulphates**, qualitative reactions, II. 574*d*  
**Persulphocyanogen**, II. 261*b*  
**Pertite**, explosive, IV. 476*d*  
**Peruresinotannol**, I. 616*c*  
**Peruvial**, I. 616*c*  
**Perylene**, I. 426*d*  
**Petalite**, II. 195*c*  
**Petaloxanthin**, II. 399*d*  
**Petermann solution**, V. 81*a*  
**Petit grant**, II. 137*d*  
 "**Petroklastit**," IV. 464*a*  
**Petroleum**, acids from oxidation, I. 120*b*  
 — and shale oil, V. 379*a*  
 —, aromatic hydrocarbons in, I. 466*c*  
 —, cracked, hydration of olefins from, II. 428*b*, 471*d*  
 —, hydrogenation, II. 425*d*  
 — in cassia oil, test for, II. 419*a*  
 —, origin, II. 280*c*  
 — sulphonic acids, IV. 288*b*  
**Petunin**, III. 554*d*; VI. 93*a*  
**Pe-tun-tse**, III. 32*d*  
**Petunzite**, III. 32*d*  
**Petzite**, VI. 102*a*, 200*a*  
**P. and P.H. Helmet**, III. 18*b*  
**Phenethine**, P.-methine base, VI. 496*c*; II. 481*b*  
**Phosphoribides**, III. 81*d*  
**Phosphophytin**, III. 81*d*  
**Phagocytes** of blood, II. 20*a*  
 "**Phanodorn**," I. 623*a*  
**Pharbitinic acid**, VI. 93*b*  
**Pharmacolite**, II. 226*b*  
**Phaseolin**, III. 414*a*  
**Phaseolunatin**, VI. 91*a*  
**Phase test** for chlorophyll, III. 84*d*  
 pH, definition, II. 638*b*  
**Phasants eye**, I. 145*b*  
**Phellandrene**, I. 5*c*  
 — in essential oils, II. 25*b*, 249*b*; III. 183*b*, *c*  
**Phellonic acid**, III. 360*a*  
**Phenacyl esters**, II. 378*b*  
 —, *p*-bromo-, II. 378*a*  
**Phenakite**, I. 685*a*; VI. 13*c*  
**Phenan**, III. 328*c*  
**Phenanthranaphthazine**, I. 568*a*  
**Phenanthraphenazines**, I. 567*d*  
**Phenanthraquinone** phosphor, II. 224*b*  
 —, reaction with  $\alpha$ -diamines, I. 567*d*  
**Phenanthrene**, detection in anthracene, I. 387*c*  
**Phenarsazines**, I. 494*d*  
 "**Phenaspetin**," I. 518*b*  
**Phenazine**, see Quinoxalines.  
 "**Phenazone**," I. 449*a*  
 "**Phenazopyrine**," I. 73*b*  
**Phenagol**, IV. 257*c*  
**Phenetole**, *p*-amino-, I. 307*c*  
 "**Phenobarbital**," I. 623*a*  
 "**Phenocain**," VI. 240*b*  
**Phenol** (see also Carboic acid), II. 303*d*  
**Phenol**,  $\alpha$ -bromo-, conversion into catechol, II. 430*b*  
 —, bromo-derivs., II. 307*a*  
 —,  $\alpha$ -chloro-, in catechol prepn., II. 430*b*  
 —, detection and detn., II. 307*b*, 570*c*, 708*b*  
 —, dinitro-, II. 306*d*; IV. 475*d*  
**Phenoldisulphonic acid**, catechol from, II. 430*b*  
**Phenol-formaldehyde resins**, II. 422*d*  
 — from acetylene, I. 83*d*  
 — in castor, II. 419*d*  
 —, iodo-, II. 307*a*  
 "**Phenol**, liquefied," II. 305*d*  
**Phenolphthalein**, prepn., II. 307*b*  
 —, tetraiodo-, sodium salt, I. 448*d*  
**Phenol** production from coal, II. 303*d*  
 —, purification with aromatic sulphonic acids, II. 304*d*  
 —, reaction with Millon's reagent, II. 307*c*  
 —, recovery, II. 319*d*  
 — resins, II. 308*d*  
**Phenols**, carboxylic acids from, II. 304*b*  
 —, chloro-, prepn., II. 307*a*  
 —, luminescent oxidation, III. 23*c*  
 —, nitro-, IV. 475*c*  
 —, —, explosives, IV. 475*c*  
 —, —, formation, II. 306*d*  
**Phenolsulphonic acids**, II. 307*a*  
 —, synthetic, II. 304*d*  
**Phenoltetrabromophthalein**, disodium sulphionate, II. 118*d*

- Phenol**, trinitro-, *see* Picric acid.  
**Phenonaphthacridine**,  $\alpha$ - and  $\beta$ -, I. 129c  
 -- carboxylic acid, I. 129c  
**Phenonaphthacridines**, 1. 129c  
**Phenonaphthacridones**, 1. 129d  
**Phenonaphthazine**, I. 564d  
**Phenosafrafranine**, I. 571c, 573b  
**Phenoxyacetic acid**, 2-carboxy-5-methoxy-, II. 69c  
**Phenylacridine**, 2-amino-8-dimethylamino-5-*p*-dimethylamino-, I. 133b, c  
 --, 2,8-dimethyldiamino-, 1. 133c  
 **$\beta$ -Phenylacrylic acid**, III. 180c  
**Phenylalanine**, 3:4-dihydroxy-, I. 317d; V. 87b  
**Phenylarsonic acid**, I. 485b  
 --, 3-acetylarnido-4-hydroxy-, I. 39c, 489c  
 --, *p*-amino-, I. 486c  
 --, *p*-carbamino-, I. 487a  
 --, diamino-, I. 488b  
 --, hydroxyamino-, I. 489b  
**1-Phenylbenzotriazole**, II. 278c  
**Phenyl isobornylamine**, II. 258c  
 carbonylamine chloride production, III. 17a  
 -- cerotate, II. 516c  
**Phenylchromone**, 2- and 3-, V. 255a, c  
**Phenylcinchoninic acid** (*see also* Cinchophen), III. 178d  
**Phenylcoumarin**, hydroxy-, II. 181c  
**Phenyl isocyanate**, reaction with hydrocarbons, II. 361a  
**Phenyldiazomethane**, III. 600a  
***o*-Phenylenediamine**, I. 565c  
***m*-Phenylenediamine**, IV. 197c  
***p*-Phenylenediamine** as hair dye, VI. 171c  
 -- dermatitis, VI. 172b  
 -- in prepn. of safranines, I. 573a  
**Phenylene-*o*-diazoinmine**, III. 593b  
***o*-Phenylenediazosulphide**, III. 593c  
***o*-Phenylenesureas**, I. 316b  
 **$\alpha$ -Phenylethyl acetate**, V. 428d  
 alcohol, VI. 429a  
**Phenylethylene**,  $\alpha$ -bromo-, II. 118d  
 **$\beta$ -Phenylglucosidase**, IV. 283c  
**Phenylglycine anilide**, I. 101b  
 -- from trichlorethylene, I. 101a  
**Phenylglyoxalic acid**, I. 71c  
 **$\alpha$ -Phenylguanidine**, VI. 146d  
**1-Phenylhydantoin**, VI. 291c  
**Phenylhydrazine**, VI. 300b  
 --, *p*-bromo-, VI. 301a  
 --, *p*-chloro-, I. 197b  
 --, detection and detn., VI. 300c  
 --, 2,4-dinitro-, I. 197a; VI. 301b  
 --, iodo-, II. 293b  
 --, *p*-nitro-, VI. 301a  
 --, reaction with carbon suboxide, II. 352d  
 -- *p*-sulphonic acid, VI. 300d  
**Phenylhydrazones**, I. 195c  
 -- of sugars, II. 292d  
 --, reaction with maleic anhydride, VI. 304a  
 --, reduction, VI. 303d  
**Phenylhydrindone**, III. 181c  
**Phenylhydroxylamine**, *p*-nitro-, III. 597b  
 **$\beta$ -Phenylhydroxylamine**, VI. 403d  
 --, nitroso-, VI. 404b  
**Phenyl -  $\beta$  - methylamino - ethanol**, 1- $\alpha$ -3:4-dihydroxy-, I. 145c  
**Phenylmethylnitramine**, trinitro-, IV. 485a  
**1 - Phenyl - 3 - methyl - 5 - pyrazolone**, I. 63d  
**Phenylnitraminoethyl nitrate**, *s*-trinitro-, IV. 488b  
**Phenyllosazone**, VI. 98c  
**Phenyllosazones**, 2:4-di-bromo-, II. 293b  
**Phenyl-peri-acid**, coupled with H-acid, IV. 204b  
***p*-Phenylphenacyl esters**, II. 378b  
**Phenyl phosphates** (*see also* Triphenyl phosphate), II. 307b  
**Phenylpropionaldehyde ethyl-acetal**, I. 36c  
 **$\beta$ -Phenylpropionic acid**,  $\beta$ -bromo-, III. 181c  
**Phenylpropyl acetate in cassia oil**, II. 418d  
**2 - Phenylquinoline - 4 - carboxylic acid**, III. 85b  
**Phenyl salicylate**, II. 307b  
 --, acetyl-*p*-amino-, II. 516d  
**4-Phenylsemicarbazide**, I. 197a; VI. 300a  
**Phenylstilbene chloride**, mono- and di-, I. 433c  
**Phenylurea**, di-*p*-carbopropoxy-, IV. 16d  
**Pheron**, IV. 317d  
 "Philanising" cotton, V. 191b  
**Philothon**, V. 23c  
**Phlobaphen**, II. 91d  
**Phloionic acid**, III. 366b  
**Phloionolic acid**, III. 366b  
**Phloraspin**, V. 181d  
**Phloridzin**, I. 451b; VI. 93b  
**Phloroglucinol** from phenol, II. 307a  
**Phloxins**, IV. 316c  
**Phocacetic acid**,  $\alpha$ - and  $\beta$ -, I. 689b, 690a  
**Phoenicic**, V. 54b  
**Phoenicite**, phornicochroite, III. 90b  
**Phorhol**, III. 434d  
**Phormium**, II. 461b  
**Phormium tenax**, V. 105b  
**Phorone**, I. 66d  
**Phosgenation** of dyestuff mixtures, IV. 222a  
**Phosgene** (*see also* Carbonyl chloride), II. 321c  
 --, detection and detn., II. 322a, 685a  
 -- in warfare, III. 9a  
 --, reaction with hydrocarbons, II. 304a  
 --, prepn., II. 350d, 428d; III. 17a  
**Phosphagen** or phosphocreatine, III. 415b  
**Phosphatase**, II. 296a; IV. 314b  
 --, bone, II. 27d  
 -- in malting, II. 89a  
**Phosphate**, African, V. 69b  
 --, "available," detn., American method, V. 81a  
 --, Belgian and Somme, V. 68b  
 --, Christmas Island, V. 69c  
 -- coating of iron, III. 392d  
 -- deficiency in grass land, VI. 133a  
 --, detn., *see also* Phosphoric acid, detn.  
 --, colorimetric, II. 674a  
 --, gravimetric, II. 598d  
 --, micro-methods, II. 633a  
 --, potentiometric, II. 700c  
 --, volumetric, II. 605a  
 --, drop reaction, II. 582b  
 --, Florida, V. 69b  
 -- in flour, II. 70c, 81a  
 --, Pacific, V. 69c  
 --, precipitated, fertiliser, V. 67c  
 --, reverted, detn. in superphosphate, V. 80d  
 --, Rhennania, V. 67d  
**Phosphates**, Caribbean, V. 68d  
 --, ground mineral, V. 69d  
 -- in casein paints, II. 415c  
 --, mineral, detn. of Mg and Al in, V. 78b  
 --, organic, in fire extinguishers, II. 350c  
**Phosphate**, South Carolina, V. 68b  
**Phosphates**, qualitative reactions, II. 552a, 555d, 557c, 572d  
**Phosphate**, total, detn. in fertilisers, V. 79d  
**Phosphatic rocks** for superphosphate manufacture, V. 68a  
**Phosphatide** of cabbage, II. 183a  
**Phosphatides**, VI. 69d, 70b  
 -- in cacao butter, II. 186a  
 --, flour, II. 78a  
**Phosphine**, detection, II. 685b  
 fumigation, V. 397d  
**Phosphines**, Brilliant, I. 132c  
 --, Patent, I. 132c  
 --, Pharma, I. 132d  
**Phosphites**, qualitative reactions, II. 573a  
**Phosphoamino-lipids**, VI. 66d  
**Phosphocreatine**, VI. 75b  
**Phosphoesterases** of bran, II. 60d  
**Phosphoglyceraldehyde** and acetaldehyde, oxido-reduction, V. 33d  
 -- transformation in muscle, VI. 76d  
**Phosphoglyceric acid**, formation by yeast, II. 99d  
 -- acids in muscle or yeast, V. 25a  
**Phosphoglycerol**, V. 25a  
 -- and pyruvic acid, oxido-reduction, V. 34a  
**Phosphoglyceromutase**, VI. 77a  
**Phosphohexomutase**, V. 36d  
**Phospholipins**, VI. 69d  
**Phosphomolybdic acid**, catalyst for acetic acid prepn., I. 350d

- Phosphoprotein** in mammalian milk, II. 411b  
**Phosphopyruvic acid**, V. 27b; VI. 77a  
**Phosphor-bronze**, III. 355b  
 —copper, III. 355b  
**Phosphorescence**, III. 23a  
 —of calcium nitrate, II. 222c  
 —sulphide, II. 230a  
**Phosphoric acid** catalyst for acetic acid prepn., II. 350d  
 —, citrate-soluble, V. 81a  
 —, —, detn., V. 82c  
 —, dehydrating catalyst, II. 428b  
 —, detn., *see also* Phosphate, detn.  
 —, —, citric-oxalic-Mg method, V. 77a  
 —, —, in mineral phosphates, V. 75c  
 —, —, Jorgensen method, V. 70a  
 —, —, of citrate-soluble, V. 81a, 82a  
 —, —, total, in basic slag, VI. 81d  
 —, —, —, fertilizer, VI. 79d  
 —, —, rapid method with magnesium, V. 78a  
 —, —, St. Gobain (Santfourche) method, V. 70b  
 —, removal in analysis, II. 552b  
 —esters of fermentation and muscle extract, *see* Fermentation, alcoholic; Glycolysis.  
 —, —, sugars, II. 295d  
 —, —, plasticisers, II. 448c, 472c  
 —oxide for glassmaking, V. 560a  
**Phosphorites** for superphosphate manufacture, V. 68c  
**Phosphorous acid**, qualitative reactions, II. 573a  
 —, detn. volumetric, II. 665c  
**Phosphors**, boric acid, II. 46d  
**Phosphorus carbide**, II. 281a  
 —chloride as chlorine carrier, II. 353b  
 —, detn., assay, I. 531c  
 —, in carbon compounds, II. 622c  
 —, —, iron and steel, II. 599a, 605b  
 —, —, micro-method, II. 633a  
 —, —, in calcium carbide, II. 216d  
 —elemental, detection, II. 572d, 685b  
 —, —, detn., volumetric, II. 665c  
 —in casein, II. 412b  
 —stainless steel, detn., II. 599b  
 —, luminescence, III. 23b  
 —, organic, in rice, II. 498d  
**Phosphorylation** by co-enzyme, V. 38b  
 —inorganic phosphate, V. 36a  
 —the adenylic acid system, V. 34d  
 —yeast preparations, V. 37d  
 —in alcoholic fermentation, V. 35d  
 —lactic acid formation, V. 34d  
**Phosphorylation** in living yeast, V. 40c  
**Phosphotriose** dehydrogenase, V. 33a  
 —, phosphoglyceric acid and phosphoglycerol from, V. 33b  
 "Phosphuret of baryta," I. 643a  
**Photographic film**, II. 446a  
 —paper, "diazotype," III. 590a  
 —, "ozalide" or "ozalid," III. 589d  
**Photo-sensitization** of combustion, IV. 418b  
**Photosynthesis** of carotenoids, II. 402a  
**Phototropy** of calcium sulphide, II. 230a  
**Phrenosin**, II. 506c; VI. 93c  
**Phthalhydrazide**, 3-amino-, luminescence, III. 23d  
**Phthalic acid esters**, as plasticisers, II. 448c, 472c  
 —anhydride production, II. 428a  
**Phthalimide**, alkyl derivs., I. 309a  
**Phthalocyanines**, co-ordination formulae, III. 332d  
 "Phulwa," I. 654a  
**Phulwara butter**, I. 654a  
**Phycocyan**, I. 200b, 692a  
**Phycocyanobilin**, I. 200c  
**Phycocerythrin**, I. 200b, 692a  
**Phycocerythrobilin**, I. 200c  
**Phycophain**, I. 199c, 200a  
**Phyllanthin**, VI. 93c  
**Phylloestrioporphyrin**, III. 82d  
**Phyllocalaine**, VI. 138c  
**Phylloerythrin**, III. 84b  
**Phylloporphyrin**, III. 82d  
 —, relation to blood pigments, II. 20c  
**Phyllopyrrole**, III. 83b  
**Physalien**, II. 398d  
**Physcion**, V. 54d  
**Physical determinations**, micro-methods, II. 634b  
**Physic nut oil**, III. 460c  
**Physostigmine**, II. 198d  
**isoPhysostigmine**, II. 200b  
**Physostigmol**, II. 199c  
**Physovenine**, II. 200a  
**Phytase**, II. 76b; IV. 314b  
**Phytin**, I. 198d; VI. 495c  
 —in maize, II. 482b  
 —rice, II. 499a  
**Phytol**, II. 402a  
**Phytosterolin**, VI. 93c  
**Phytosterol** in rice, II. 493d  
 —of candelilla wax, II. 262a  
**Phytosterols**, bran, II. 60b  
**Phytosterol test** of butter, II. 166d  
**Phytyl alcohol** from chlorophyll, III. 81c  
**Piassava**, V. 168a  
**Piazothiole**, I. 816b  
**Picein**, VI. 83c  
**Piceoside**, VI. 93c  
**Pickeringite**, IV. 591d  
**Picklette**, III. 77a  
**Pickling** of metals, III. 77a  
**Picoline** from acetylene, I. 84c  
**Picrates**, metallic, IV. 482c  
**Picric acid** antiseptic, IV. 30c  
 —explosives, IV. 480c, 483a  
**Picric acid** from phenol, II. 306d  
 —manufacture, IV. 476d  
 —by interdilution process, IV. 478b  
 —NaNO<sub>2</sub> process, IV. 478c  
 —continuous process, IV. 478c  
 —from chlorobenzene, IV. 479d  
 —, precautions in, IV. 482a  
 —, properties of, IV. 480c  
 —reagent for alkaloids, I. 235b  
 —, specifications, IV. 482b  
 —, testing, IV. 482b  
 —Powder, IV. 483b  
**Picrinit**, IV. 476d  
**Picrocrocin**, VI. 93d  
**Picrotonic acid**, I. 235c  
**Picryl chloride**, luminescent reaction, III. 23c  
 —sulphide explosive, IV. 481c  
**Piedmontite**, IV. 320d  
 "Pierre-à-coton," I. 500a  
**Pigment dyes**, IV. 236a  
**Pigments** for textiles, IV. 127c  
 —in butter, II. 107c  
 —casein paints, II. 415c  
 —magnesia cements, II. 136d  
 Lithol, IV. 236b  
 Monolite, IV. 236b  
 Monosol, IV. 236b  
 permanent, IV. 236b  
 polyene, II. 397d  
 "Pi-léou," III. 33b  
**Pilbarite**, VI. 155a  
**Pilchard oil**, V. 228c  
**Pilolite**, I. 499c  
**Pimelite**, V. 430a  
**Pimenta officinalis**, eugenol from, IV. 394c, 395a  
**Pimento**, II. 273b  
**Pinachrome**, III. 515b  
**Pinacone**, I. 67a  
**Pinacyanol**, III. 510c  
**Pinaflavol**, III. 530d  
**Pinaverdol**, III. 515b  
**Pinene**, borneol from, II. 31b, 257c  
 —, dibromonitroso-, IV. 2c  
 —, hydrochloride, II. 32d, 250c  
*l-α-Pinene* in cajuput oil, II. 198c  
*l-Pinene* in Canada balsam, II. 261a  
**Pinene** in essential oils, I. 5c; II. 249b, 404b; III. 183b, c  
 —peroxide, II. 251d  
 —storage, II. 250a  
 —, synthetic camphor from, II. 242b, 249c  
**Pine oil**, borneol in, II. 259b  
 —, bornyl acetate in, II. 259b  
 —in cotton bleaching, II. 6a  
**Pinitol**, I. 182c  
**Pinitol**, VI. 494c  
**Pink**, Algol, R. I. 206a, 232d, 416b  
 —, Benzo Fast, 2BL, IV. 222a  
 —, Indanthrene, FBBL, I. 418a  
 —, Naphthalene, I. 575d  
**Pinnolite**, II. 35b  
**Pinocyanol**, III. 514d, 516c  
**Pintsch-Hillebrand** generator, V. 502c

- Pinus australis*; *P. maritima*; *P. palustris*, I. 550a; V. 415c; V. 6a  
 — *picea*; *P. pumilio*; *P. sabiniana*; VI. 93d; VI. 288c; I. 1d  
 — *spp.*, turpentine and from, III. 294b  
**Pioury**, Piuri, Purree, VI. 424b  
**Piperazine**, I. 314c; IV. 376c  
**Piperidine**, I. 315a  
 — from acetylene, I. 84d  
**Piperitone**, IV. 9b  
 — in camphor oil, II. 249c  
 —, reduction, II. 426d  
**Piperylene**, II. 152b, 154c  
**Pisang** flour, I. 618d  
**Pisolite**, I. 456d  
**Pistacite**, IV. 320d  
 "Pita," I. 261b  
**Pitayo**, III. 128d  
**Pitchblende**, II. 106a; VI. 154d  
**Pittacal**, IV. 401a  
**Pityrol**, II. 60d  
 "Pi-yu," III. 33b  
 "Placidol A," I. 361a  
**Planchette**, IV. 7d  
**Plantain** fibre, I. 1a  
**Plant** analysis, ash detn., I. 503c; III. 430d  
 —, crude fibre in, III. 430c  
 —, — protein in, III. 430c  
 —, dry matter in, III. 430c  
 —, ether-soluble substance in, III. 430c  
**Plant**, chemical, resistant materials for, IV. 130b  
 "Plasmoquin," III. 137b  
 "Plastacele," II. 480b  
**Plaster**, boiled Keene's, II. 131a  
 — of Paris, II. 130b, 132a; VI. 160a  
 —, —, catalysts of set, II. 131c  
**Plasters**, calcium sulphate, II. 129b  
**Plaster-stone**, VI. 160a  
**Plasticisers** (see also Camphor; Celluloid; Cellulose plastics), II. 308d, 472b; IV. 523d  
**Plastic magnesia**, II. 136b  
**Plastics**, see also Celluloid; Cellulose plastics; Resins, synthetic.  
 , bituminous, I. 703c  
 , carbon in, II. 313a  
 , casein, II. 414b  
 , castor oil in, II. 422a  
 , nitrocellulose, II. 464b  
 "Plastolin II," I. 361a  
**Platinum** catalyst, see Catalysis; Catalyst; Hydrogenation; Reactions, heterogeneous.  
 — -chromium alloy, III. 104a  
 —, detn., II. 613a, 614b  
 —, assay, I. 528c  
 —, —, electrodeposition, II. 702a  
 —, —, gravimetric, II. 614b  
 —, —, micro-method, II. 633c  
 —, —, volumetric, II. 665d  
 — electrodeposition, IV. 270a  
 — in contact process, II. 423c  
 — nitric acid manufacture, II. 424c  
**Platinum** metals, separation and detn., II. 613a, 614a  
 —, qualitative reactions, II. 554d, 556d, 579b  
**Pleochroism** of bromine, II. 107d  
**Plumbago**, II. 309b, d. 313d  
**Plumbous** acetylide, II. 281c  
**Plumosite**, IV. 591d  
**Plusinglanz**, I. 466a  
**Podolite**, I. 449d  
**Polar** and non-polar links, III. 334a  
**Polar** Dynobel, IV. 556d  
**Polarisation**, molecular, VI. 406b  
**Polarographic** analysis, II. 710b  
 "Polaroid," V. 596a  
**Polar** Samsonite No. 3, IV. 55b  
 — Saxonite, IV. 556d  
**Polenske** value of butter, II. 165d  
 — — — cacao butter, II. 185b  
**Polierschiefer**, III. 579c  
**Pollucite**, II. 195c  
**Pollux**, II. 195c  
**Polyalkylguanidines**, VI. 116d  
**Polyanthrimsides**, I. 449d  
**Polychloroprene**,  $\alpha$ - and  $\mu$ -, I. 89b  
**Polycrase**, II. 19c, 512c  
**Polynes**, geometric isomerism, II. 151c  
**Polygalritol**, II. 296c  
**Polyglycerol**, VI. 70c  
**Polymerisation**, see also individual aldehydes.  
 , catalytic, II. 429a  
 , metal carbonyls as catalysts in, II. 358d  
 — of acetylene, I. 85b  
 — of olefins, II. 153b  
 — unsaturated glycerides, IV. 89d  
**Polyolefins** (conjugated), II. 151a  
 — (non-conjugated) II. 150b  
**Polyoxymethylene**,  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\epsilon$ -, V. 319a  
 — compounds, II. 158d  
**Polypeptidases**, IV. 315a, 325a  
**Polyporus** spp., IV. 282c  
**Polyprenes**, II. 154a  
**Polysaccharides** (see also Cellulose), II. 301c  
 —, chain length, II. 301d, 458a  
**Polystichin**, V. 182a  
**Polythionic** acids, detn., volumetric, II. 667b  
**Polyuronic** acid, II. 298a  
 "Polyzyme," V. 59c  
**Polyzoa**, coral from, III. 300c  
**Pomace**, II. 452c; III. 124d  
**Pomegranate** seed oil, IV. 86d  
 "Pomelo," VI. 129b  
**Pomeranz-Fritsch** synthesis, VI. 188c  
**Pomilio** electrolytic cell, III. 54a  
**Pontianak** Illipé nuts, II. 31d  
 — substitute, II. 119a  
**Poppy** seed oil, IV. 85d  
**Populin**, VI. 93d  
**Populinin**, VI. 94a  
**Porphin**, III. 82c; VI. 104a  
**Porphyrene**, I. 263c  
**Porphyrin** in catalase, II. 422c  
**Porphyryns**, II. 20b; III. 82d; VI. 161c  
 —, identification, VI. 164a  
 —, metallic derivs., VI. 104a  
 —, synthesis, VI. 163a  
**Porphyrite**, III. 32d  
**Portland** blast-furnace cement, II. 145a  
 — cement (see also Cement), II. 140d  
 —, —, Eisen-, II. 145b  
 —, —, setting, II. 229b  
 — stone, V. 329b  
**Positron**, I. 512d  
**Potash**, detn. in fertilisers, V. 82b  
 — felspar for glassmaking, V. 561b  
**Potassium** antimonyl tartrate, I. 448b  
 — argentocyanide, III. 187c  
 — barium ferrocyanide, III. 170c  
 — bromate in flour, II. 81d  
 — calcium ferrocyanide, III. 470d  
 — carbide, II. 280d  
 — carbonate for glassmaking, V. 561a  
 — carbonyl, II. 357c  
 — carbonylferrocyanide, III. 476b  
 — chloride in carnallite, II. 390a  
 — chromate, III. 110b  
 — cobaltinitrite, III. 219b  
 — cyanate, III. 507b  
 — cyanide, III. 484b  
 —, detn. as  $KClO_4$ , II. 584d; V. 82c  
 —, —, cobaltinitrite method, V. 83a  
 —, —, in clay, III. 203c  
 —, —, volumetric, II. 665d  
 —, — with  $PtCl_4$ , II. 584c; V. 82d  
 — dichromate, III. 110c  
 — drop reaction, II. 581a  
 — ferricyanide, III. 470a  
 — ferrocyanide, III. 474d  
 — ferrous ferrocyanide, III. 471c  
 — fluoroborate (native), I. 560c  
 — hydrogen tartrate, I. 461d  
 — hypoborate, II. 45d  
 — hypochlorite, III. 61c  
 — metasilicate in respirators, III. 20c  
 — nitrate for gunpowder, IV. 455b  
 — perceric carbonate, II. 510d  
 "Potassium perferrocyanide," III. 477c  
**Potassium**, qualitative reactions, II. 551c, 560a  
 —, —, rare metals present, II. 559c, 564a  
 — salts as accelerators in cements, II. 131d  
 — in bush salt, II. 150d  
 — thiocarbonate in fumigants, II. 344a  
 — thiocyanate, III. 509a  
 — vanadate in carnotite, II. 392d  
**Potato**, Namara, I. 497a  
**Potentiometric** titration, II. 702d, 704d, 705b  
 — precipitation, II. 705d  
**Pot stills**, I. 178b

- Potstone**, building, II. 138a  
**"Potters' ore,"** V. 415d  
**Potter's stone**, VI. 180b  
**Pottery**, colouring (*see also* Glazes and frits), II. 194b; III. 220a  
**Poudre B**, manufacture, IV. 518a, 526b  
**Poudres** Designolle, IV. 476b, 483a  
**Pouring** of candles, II. 265c  
**Pousse**, III. 127a  
**Powder** of Algaroth, I. 446b, 448a  
**Powders**, particle size, IV. 98a  
**Pozzolanas**, Pozzolanic cements, II. 145c  
**"Pragmolin,"** I. 73b  
**Praseodymium**, II. 511c  
 — in ceric oxide, II. 510a  
**Pratensol**, III. 206c  
**Pratol**, III. 206a  
**"Prayer Beads,"** I. 4c  
**Precipitation** in analysis, II. 543b  
**Precipitin** of blood, II. 22b  
**alloPregnane**, VI. 277b  
**Prehnite**, VI. 136d  
**Prehnite**, III. 539a  
**Premier jus**, IV. 253b  
**Preservation**, food, V. 290b  
**Preservatives**, food, V. 296a  
 — in butter (*see also* Food preservatives), II. 167d  
 —, natural occurrence, V. 306b  
 — of stone, II. 139d  
**Pressure** effect on compressibility and thermal expansion of liquids, VI. 227a  
**Priceite**, II. 48c; III. 278c  
**Prill**, I. 525b  
**Primerverase**, IV. 314b  
**Primeverin**, II. 300b; VI. 94a  
**Primeverose**, II. 298b  
**Priming** (explosive), IV. 485a  
**Primula officinalis**; *P. spp.*, VI. 91d, 94a, 230c  
 — *spp.* enzymes, V. 416d  
 —, flavone from, V. 257b  
**Primulaverin**, II. 300b; VI. 94a  
**Primulin**, anthocyanin, III. 554c  
**Primuline**, dye, IV. 225b  
**Printers' iron liquor**, I. 55a  
**Printing**, cylinder, IV. 170a  
 —, roller, IV. 176a  
 — rollers, hand-engraved, IV. 176a  
 — textiles, *see* Textile printing.  
**Priorite**, II. 19c  
**Prismatic powder**, IV. 458d  
**Protaine**, I. 1b, 309a; II. 34b  
**Procellose**, II. 442d  
**Producer-gas**, II. 345a; V. 367c  
 —, ammonia recovery, V. 373d  
 —, blowers, V. 373a  
 —, cleaning and cooling, V. 373a, 374d, 377a  
 —, grates and plant, V. 369b  
 — in ammonia production, II. 424a  
**Producers**, gas-, revolving, V. 370d  
**Proflavine**, antiseptic, I. 134a; IV. 30b  
**Progesterone**, VI. 272c, 273a, 274b  
**Progressive burning powders**, IV. 527a  
**Prolamines**, rice, II. 493b  
**Prolan A**, Prolan B, VI. 266d  
**Proline**, I. 886c  
**Prométhée**, IV. 545c  
**"Prominal,"** I. 623a  
**Promoter** action, VI. 259a, 355c  
**Promoters** (flotation process), V. 263d  
**Proof spirit**, sp.gr. and definition, I. 188a, 187a  
**Propaesine**, I. 369b  
**Propane**, heptachloro-, II. 321b  
**cycloPropane**, anæsthetic, I. 367d  
**Propenal**, I. 136a  
**cycloPropene**, III. 533a  
**Propene** acid, I. 137a  
 —  $\alpha$ -dicarboxylic acid, VI. 30b  
**p-Propenylanisole**, I. 371c  
**Propenylbenzene**, 3-methoxy-4-hydroxy-, IV. 397d  
**Propiolaldehyde** ethylacetal, I. 36b  
**Propiolic acid** from acetylene, I. 85a  
**Propionates**, qualitative reaction, II. 569d  
**Propionic acid**,  $\alpha$ -amino-, I. 172d  
 —,  $\beta$ -amino-, I. 175a  
 —,  $\alpha$ -amino- $\beta$ -thiol-, III. 511a  
 —,  $\beta$ -disulphido- $\alpha$ -amino-, III. 510a  
**Propionitrile**, IV. 360a  
**"Proponal,"** I. 623a  
**Propulsive strength test**, IV. 244c  
**Propylacetal**, I. 36a  
**Propylacetoacetic acid**, ethyl ester, I. 64c  
**isoPropylacetoacetic acid**, ethyl ester, I. 64c  
**isoPropyl alcohol** production, II. 426d  
**4-Propylaniline**, III. 458a  
**Propylbenzene**, *n*- and *iso*-, III. 456a  
**Propyl carbinol**, II. 169b  
**Propylcupreine**, III. 161b  
**isoPropylcupreine**, III. 161c  
**Propylene**,  $\gamma$ -bromo-, I. 257d  
 — dichloride, I. 258a  
 — from acetylene, I. 84d  
 — carbon suboxide, II. 352d  
 — oxide,  $\gamma$ -chloro-, IV. 319b  
**isoPropylethylene**, I. 364d  
**n-Propylformal**, I. 34b  
**isoPropylformal**, I. 34b  
**isoPropylhydrocupreine** hydrochloride, III. 127d  
**2-n-Propylpiperidine**, III. 325c  
**Proscillaridin A**, II. 387a; VI. 94b  
**Prosol**, II. 485b  
**Prostigmine**, II. 200d  
**Protanulin**, I. 197d  
**Protaminase**, IV. 315a  
**"Protargol,"** antiseptic, IV. 26a  
**Protease**, II. 495d; IV. 313b  
**Protection** of metals against corrosion, III. 366c, 385c  
 —, paint and allied coatings for, III. 393b  
**"Protective alkali,"** VI. 104d  
**Protective colloids**, III. 287a  
 — films on metals, III. 373c, 379b, 392a  
**"Proteolyt"** antiseptic, IV. 25d  
**Proteinase**, II. 88c  
**Proteinases**, IV. 315a  
**Protein**, Bence-Jones, and bone disease, II. 28a  
 —, casein, II. 412b  
 — in catalase, II. 422c  
**Proteins** in feeding stuffs, IV. 592a, 601d  
 —, molecular weight, III. 290b  
 —, rice, II. 493b  
**Prothrombin** in blood, II. 22c  
**Protoactinium**, I. 139c  
**Protocatechuic acid**, action of arsenic acid on, II. 439a  
 — from brazilin, II. 68d  
 — butin, II. 158a  
**Protocurarine**, III. 460b  
**Protocuridine** and proto-curine, III. 160b  
**Protohæmin**, VI. 161d  
 —, synthesis, VI. 163a  
**Protol process**, V. 24b  
**Protoparaffin**, II. 506b  
**Protopine**, II. 527d; V. 388d  
**Protoporphyrin**, VI. 161d  
 —, relation to hæmin, VI. 161d  
**Protoquinamicine**, III. 168d  
**Prototropic changes**, VI. 256c  
**Protoveratrine**, VI. 200d  
**Provitamin D**, II. 201d  
**Prulaurasin**, I. 358a; VI. 94b  
**Prunase**, IV. 283a  
**Prunasin**, I. 358a; VI. 94b  
**Prunetin**, IV. 189b; V. 259d  
**Prunetol** or genistein, V. 259d  
**Prunetrin**, IV. 189b; V. 259d  
**Prunicyanin**, I. 449a; VI. 90d  
**Prunus amygdalis** var. *amara*, var. *dulcis*, I. 259c, 260a  
 — *spp.*, I. 452d; III. 550c; VI. 86b, 94b, 95a, d  
**Przibramite**, VI. 101a  
**Pseudoaconitine**, I. 123a  
**Pseudo-acids**, VI. 258a  
 — bases, VI. 258a  
**Pseudochalcedonite**, II. 517b  
**Pseudocorycavine**, III. 402c  
**Psicaine**, I. 369a; III. 225d  
**Psittacinite**, III. 560b  
**Psoralene**, V. 171a  
**Psychotrine**, IV. 281a  
 — *o*-methyl ether, IV. 281a  
**Psychrometer**, Assmann, VI. 285d  
 —, sling, VI. 285d  
 —, whirling, VI. 285d  
**Ptychotis oil**, I. 172a  
**Puberulic acid**, V. 56  
**Pucherite**, I. 694a  
**Pulas**, II. 157d  
**isoPulegol**, III. 162d  
 — acetate, III. 102b  
**Pulfrich photometer**, III. 304d  
**Pulp conditioners**, V. 265d  
**Pulque**, I. 165a  
**Pulvis algarothi**, I. 448a  
 — *angelicus*, I. 448a  
 — *Carthusianorum*, I. 446c  
**Pumice**, I. 4c  
**Pumps**, high vacuum, III. 605a  
 —, measuring, for rayon spinning, V. 116d, 119a, 123c  
**Punica granatum**, IV. 258a; VI. 94b

- Punicic acid**, IV. 258a  
**Punicin**, VI. 94b  
**Purging nut oil**, III. 400c  
**Purine**, II. 198b  
 —, 6-amino-, I. 141b; II. 198a  
 —, 2,6-dihydroxy-, II. 198b  
 —, 6-hydroxy-, II. 198b  
**Purines** in nucleotides, II. 287b  
**Purple**, Caledon Brilliant, 4R, I. 421b, 429d  
 — copper-ore, II. 32d  
 — of Cassius, II. 419c; V. 513c; VI. 122b  
 — the Ancients, VI. 452c  
 — "Purple, Perkin's," I. 577c  
**Purple**, Soledon, 2H, I. 429b  
 —, Thiazole, III. 514d, 518c  
 —, Tyrian, I. 577c; II. 107d; VI. 452c  
**Purpurea** glycoside A, B, VI. 94b, c  
**Purpurin**, I. 200a, 212d, 223d, 402c  
*isoPurpurin*, see Anthrapurpurin  
**Purpurinamide**, I. 224b  
**Purpurin-3-carboxylic acid**, V. 415c  
 —, 3-chloro-, I. 224b  
 —, 3,5-disulphonic acid, I. 224b  
 —, 3-monosulphonic acid, I. 390b  
 —, 3-nitro-, I. 392d  
 —, triacetate, I. 224b  
**Purpuroxanthin**, I. 212d, 220c  
 —, dichloro-, I. 224c  
**Purrenone**, purrene, VI. 424c  
**Putrescine**, II. 178c; IV. 331d  
 — "Pygodantin," I. 548d; IV. 30b  
**Pyraconine**, I. 121c  
**Pyraconine**, I. 121c, 122a  
 — "Pyralin," II. 443b, 480b  
 — "Pyramidone," I. 305a; VI. 300d  
**Pyranose** sugars, II. 282d  
**Pyranthridone**, I. 400a  
**Pyranthrone**, discovery, synthesis, I. 413c, 426d  
 — dyes, I. 205c, 399c, 419d  
**Pyrrargyrite**, I. 439d  
**Pyrazine**, I. 504b, d  
**Pyrazoleanthrone**, I. 409d  
**Pyrazolediazonium salts**, III. 592a  
 — "Pyricat" disinfectant, IV. 22d  
**Pyridinearsonic acids**, I. 490a  
**Pyridine** as insecticide, IV. 31b  
 —,  $\beta$ -carboxydiethylamide, II. 203b  
 — complexes with catechol, II. II. 431a  
 —, 3,4-dicarboxylic acid, III. 127d  
 — in fumigants, II. 344a  
 —, recovery from carbohic acid, II. 304b  
 —, reduction, II. 427b  
 — 2,2'- and 2,4'-Pyridocarbo-cyanines, III. 522a  
**2-Pyridone-5-arsonic acid**, sodium salt, I. 490b  
**1,3-Pyrimidinetrone**, I. 243d  
**Pyrite**, IV. 279d  
**Pyrites** gases, purification, II. 423c  
 — "Pyrobor," V. 559d  
**Pyroboric acid**, II. 47a, d  
**Pyrocalciferol**, II. 202a  
*isoPyrocalciferol*, II. 202a  
**Pyrocatechol**, I. 505d; II. 429c  
 — from phenol, II. 307a  
 —, methyl cetyl ether, II. 516d  
**Pyrochlore**, III. 310a  
**Pyrogallol**, antiseptic, IV. 29c  
 — methyl ether, oxidation, II. 440d  
 — monoacetate, IV. 394b  
 —, qualitative reactions, II. 570c  
 —, reagent, II. 078a  
**Pyroglycerin**, IV. 491d  
**Pyroindacitine**, I. 123a  
**Pyroligneous acid**, preservative, V. 297a  
 —, production, I. 48b; II. 310d  
**Pyromellitic acid** from charcoal, II. 310c  
**Pyrometers**, colour brightness, V. 241b  
**Pyromucic acid**, V. 401c  
 — aldehyde, V. 400c  
**Pyrope**, V. 429b  
**Pyrophorus**, Homberg's, I. 290a  
**Pyrophyllite**, I. 162c; III. 106a  
**Pyropseudacitine**, I. 123b  
**Pyrrhite**, II. 512b  
 — "Pyrosal," I. 73b  
**Pyrotachysterol**, II. 202a  
**Pyroxylin** lacquers, II. 467d  
**Pyroetioporphyrin**, III. 82d  
**Pyrrroles**, formation from chlorophyll, III. 83b  
**Pyrrolidine**, I. 315a  
*l*-**Pyrrolidone-2-carboxylic acid**, VI. 33b  
**Pyrrorporphyrin**, III. 82d  
**Pyruvic acid** in muscle, VI. 70c  
 — from cereals, II. 487b  
 — moulds, V. 50d  
 — yeast, II. 99b
- Q**
- Quacahault**, III. 230d  
**Quadridentate groups**, III. 320d  
**Quartz**, I. 4c  
 — glass, V. 605d  
 —, II. 517b  
 —, I. 4c  
 — rock, I. 4c  
 — rachtol, VI. 494c, 405d  
 — "Queensland arrowroot," I. 468b  
 — etagetin, I. 161b  
 — etagetic acid, 161c  
 — etin, III. 405a  
 — occurrence, I. 409a; II. 120c, 234d, 434b  
**Quercimeritrin**, III. 406a; VI. 94c  
*isoQuercimeritrin*, VI. 94c  
**Quercine**, III. 244b  
 —, tol, VI. 495d  
 —, tin, see Quercetin.  
 —, tol, *d*-, and *l*-, VI. 496a, b  
 —, itrin, *isoquercitrin*, III. 405a, 406c; VI. 94c  
**Quercitron** bark, III. 405a; IV. 128c  
**Quercus agilops**, IV. 270d; V. 417a  
**Quercus** spp., cork from, III. 365b  
 —, galls from, V. 425a, 420a  
 — *tincitoria*, VI. 94c  
**Quicksands**, explanation, III. 292b  
**Quillaia saponaria**, VI. 94d  
**Quillaia-saponin**, VI. 94d  
 — "Quina," III. 172b  
**Quinaldine** from acetylene, I. 84c  
**Quinaldinic acid**, reagent, II. 583c  
**Quinalizarin**, prepn., I. 213a, 402c  
 —, properties, I. 220b  
**Quinacrine**, III. 168d  
**Quinacridine**, III. 168d  
**Quinamine**, III. 128a, 160c, 168c  
*apoQuinamine*, III. 169a  
**Quinisoamyline**, III. 161c  
 — "Quinaphenin," III. 33a  
**Quinazocarbocyanine**, III. 523a  
**Quinene**, III. 138b, 177d  
**Quinethyline**, III. 161b  
**Quinetum**, III. 160a  
**Quinic acid**, III. 79d  
**Quinicine**, III. 128a, 170d  
**Quinidine**, III. 128a, 152c, 160b  
 —, acetyl-, III. 170b  
 —  $\alpha$ -*isoQuinidine*, III. 170d  
*isoapoQuinidine*, III. 170d, 171c  
*neoisoQuinidine*, III. 171a  
**Quininal**, III. 140a, 178a  
**Quinine**, III. 128a, 172b  
 —, acetyl-, III. 174c  
 —, benzoyl-, III. 174c  
 —,  $\alpha$ -bromohydro-, III. 175b  
 —, carbophenetidine, III. 33a  
 —, diethylbarbiturate, III. 83a  
 —, ethyl carbonate, IV. 401d  
 —, formate, III. 33d  
 —, idiosyncrasy, III. 170a  
 —, urea, III. 137b  
 —, urethane, III. 137b  
*epiQuinine*, III. 128a  
*isoQuinine*, III. 173a, 175d  
*isoapoQuinine*, III. 176d  
*pseudoQuinine*, III. 175d  
**Quinonic acid**, III. 138a, 144a, 178b  
 —, synthesis, III. 144a  
**Quinonone**, III. 138b, 177c  
 — "Quinisal," III. 174a  
 — "Quinisan," III. 174a  
**Quinizarin**, I. 212d, 220d, 402c  
 — dibromo-, I. 221c  
 — 5:6-dichloro-, I. 221d  
 — 5:8- and 6:7-dichloro-, I. 221d  
 — 2-nitro-, I. 221c, 392c  
 — relationships, I. 206c  
 — 2-sulphonic acid, I. 221c, 457c  
 — "Quinodine," III. 161d  
 — "Quinoform," III. 174a  
 — "Quinoidine," III. 162a, 169c, 178d  
**Quinol**, VI. 399a  
 — 4-carboxylic acid, VI. 262a  
 — dimethyl ether, IV. 6d  
 —, hydroxy-, VI. 404d  
**Quinoline**, 8-hydroxy-, reagent, see Oxine.  
 —, salicylic ester, I. 171d

- Quinolinesulphonic acid**, iodo-hydroxy-, III. 33*d*  
 —, iodoxy-, I. 370*a*  
**Quinoline-5-sulphonic acid**, 8-hydroxy-, III. 33*d*  
**Quinones**, compounds with maleic anhydride, II. 153*b*  
**Quinonoid** theory of colour, III. 308*d*  
 — structure, *o*- and *p*-, I. 570*d*  
**Quinophan**, III. 85*a*  
**"Quinosol,"** III. 33*d*  
**Quinotoxine**, III. 128*a*, 176*d*  
**"Quinotropin,"** III. 33*d*  
**Quinovatine**, III. 151*c*  
**Quinovose**, II. 287*c*; IV. 321*a*  
**Quinoxalines**, I. 316*b*, 563*d*, 565*c*  
 —, diamino-, I. 316*b*  
 —, dihydroxy-, I. 316*b*  
**Quinisopropyline**, III. 161*b*  
**Quinuclidine**, III. 141*d*  
**Quitenidine**, III. 139*d*, 172*b*  
**Quitenine**, III. 34*a*, 130*d*, 178*a*  
 "Quitenol," III. 178*b*
- Racemisation**, rate, VI. 257*b*  
**Rackarock** and rackarock special, IV. 465*b*, 545*c*  
**Radium** in carnotite, II. 393*a*  
**Radix liquoritiae**, VI. 91*b*  
 — *aarsaparilla*, VI. 95*c*  
**Raffia**, V. 168*b*  
**Raffinase**, V. 9*d*  
**Raffinose**, II. 282*b*, 301*c*  
 —, colour reaction, II. 300*b*  
 —, hydrolysis, II. 299*c*; VI. 395*c*  
*gl*, II. 482*d*, 488*d*  
 —, ultimes, II. 690*a*
- **Raisin-seed oil**, R.-pip oil, VI. 130*c*  
**Ramie** (China grass), II. 461*b*; III. 31*c*; V. 163*b*  
 — fibres, X-ray diagram, II. 301*c*  
**Ramsden's** membranes, IV. 285*a*  
**Randannite**, III. 578*d*  
**"Raney nickel,"** VI. 181*d*  
**Raoult's** law of vapour pressures, IV. 30*c*, 47*d*, 48*b*  
**Raphia** spp., V. 168*a*  
**"Rapid fast"** colours in azoic dyes, IV. 233*a*  
**"Rapidogen"** azoic dyes, IV. 233*b*
- Raseneisenstein**, II. 20*a*  
**Rasgrite**, II. 40*a*, 49*a*  
 —, borax manufacture from, II. 46*d*  
**Rast** freezing-point method, III. 443*c*  
**Rati**, I. 4*c*  
**Rats**, fumigation against, V. 394*c*, 395*a*  
**Ravenelin**, V. 55*d*  
**X-Ray** contrast media, I. 4*c*; VI. 464*a*  
 — photography, II. 451*b*  
**Rayon** (see also Artificial silk), V. 112*a*, 114*a*  
 —, animalised, IV. 125*c*  
 — cake treatment, V. 121*a*  
 —, cellulose acetate, II. 564*d*; V. 113*b*
- Rayon**, Chardonnnet nitrate, II. 464*b*; V. 113*a*, 114*d*  
 —, continuous production, V. 126*d*  
 —, crêpe fabrics, V. 121*d*  
 —, delustring or matting, V. 202*a*  
 —, dyeing, IV. 124*c*, 137*c*  
 —, printing on, IV. 187*d*  
**Rayons**, breaking strength and extensibility, V. 130*c*  
 — coloured in the spinning mass, IV. 139*b*  
 —, elasticity, V. 132*c*  
 —, fixing acid dyes, V. 128*c*  
 —, identification, V. 133*b*  
**Rayon** spinning devices, V. 116*d*, 117*a*, 119*a*, 123*c*  
 — staple fibres, IV. 125*a*; V. 113*c*, 127*c*, 131*d*  
**Rayons**, stretch spinning, see Stretch-spinning of rayon.  
 —, structure, V. 128*c*, 130*a*  
 —, wet strength, V. 131*a*  
**Rayon**, viscose, chain length, II. 301*d*  
 — with reduced lustre, V. 128*c*  
 — yarns, continuous filament, V. 112*b*
- Reaction**, see also Catalysis; Catalysts; Esterification, catalytic; Reactions, heterogeneous.  
**Reaction** energies, heterogeneous and homogeneous, compared, VI. 212*b*  
 — kinetics, II. 533*a*  
**Reactions**, exchange, VI. 219*d*  
 —, heterogeneous (see also Adsorption; Catalysis, Hydrogenation), VI. 207*b*  
 —, —, activated adsorption in, VI. 214*b*  
 —, —, activation energy, VI. 210*b*, 213*b*  
 —, — and homogenous, compared, VI. 211*d*  
 —, —, at gas-liquid interfaces, VI. 219*c*  
 —, —, — liquid-liquid interfaces, VI. 222*b*  
 —, —, — solid-liquid interfaces, VI. 215*b*, 217*a*  
 —, —, — solid-solid interfaces, VI. 223*b*  
 —, —, — the interface, VI. 221*c*  
 —, —, base-exchange, VI. 218*b*, 219*a*  
 —, —, — capacity, VI. 219*a*  
 —, —, bimolecular processes, VI. 209*a*, 212*a*  
 —, —, catalysts, massive and colloidal, VI. 216*c*  
 —, —, chemisorption, VI. 214*b*  
 —, —, distribution equilibria, VI. 222*b*  
 —, —, induction period, VI. 223*b*  
 —, —, inhomogeneity of surfaces, VI. 211*b*  
 —, —, kinetic velocities, VI. 214*a*  
 —, —, liquid phase, VI. 222*c*  
 —, —, mineral exchangers, VI. 219*b*  
 —, —, of isotopic molecules, VI. 213*d*  
 —, —, rate-controlling processes, VI. 215*c*, 218*d*
- Reactions**, heterogeneous, on saturated surfaces, V. 211*a*  
 —, —, order, VI. 210*b*  
 —, —, temperature coefficient (see also Reaction velocity), VI. 216*b*  
 —, —, tunnel effect, VI. 214*c*  
 —, —, unimolecular, VI. 208*a*, 210*a*  
 —, —, velocities (see also Reaction velocity), VI. 213*b*  
 —, —, zero-point energy, VI. 214*c*  
 —, —, high pressure, VI. 226*c*  
 —, —, — polymerisations in, VI. 229*d*  
 —, —, —, velocity constants, VI. 228*b*
- Reaction**, spontaneous, VI. 212*c*, 255*d*  
 — velocity, bimolecular (see also Reactions, heterogeneous), II. 532*c*  
 —, —, temperature effect (see also Reactions, heterogeneous), II. 533*a*  
 —, —, trimolecular, II. 533*a*  
 —, —, unimolecular, II. 530*a*
- Realgar**, I. 468*c*  
**"Recidon,"** I. 625*a*  
**Red**, Alcol. RTK, FF, I. 420*c*, 232*d*  
 —, Alizarin, I. 200*a*  
 —, —, S, WS, 3WS, I. 220*d*, 230*b*  
 —, Antimony, I. 430*d*  
 —, Archil, IV. 207*a*  
 —, argol, I. 461*d*  
 —, bark (cinchona), III. 128*d*  
 —, cacao, II. 188*a*  
 —, Cadmium, II. 194*b*  
 —, Caledon, BN, FF, 5G, X5B, I. 417*b*, 416*b*  
 —, —, GG, I. 427*b*  
 —, Celliton Fast, R, I. 42*a*  
 —, —, R, I. 41*b*  
 —, Chica, I. 381*d*; II. 275*c*; III. 28*b*  
 —, Chinese, I. 550*a*; III. 113*b*; VI. 12*b*  
 —, Chrome, III. 113*a*  
 —, Ciba Lake, B, VI. 451*a*  
 —, Cibanon, 4B, I. 417*a*  
 —, Cobalt, III. 219*c*  
 —, Congo, IV. 12*b*, 192*b*, 217*c*  
 —, —, indicator, II. 639*d*  
 —, Derby, I. 550*a*; III. 113*b*  
 —, Dispersol Fast, R, I. 41*a*, 42*a*
- Reddle**, VI. 161*a*  
**Red**, Erweco Acid Alizarin, BS, I. 230*a*  
 —, Ethyl, III. 515*b*  
 —, Indanthrene, BN, G and R, I. 396*b*, 414*c*, 400*b*, 420*a*  
 —, Ionamine, KA, I. 40*c*  
 —, iron-froth, VI. 161*a*  
 —, liquor, I. 54*a*, 292*d*  
 —, Magdala, I. 575*d*, 577*a*  
 —, Neutral, I. 599*c*  
 —, Nitrosamine, III. 597*b*  
 —, oil, VI. 135*b*  
 —, Para, IV. 192*d*  
 —, Peachwood, II. 74*c*  
 —, Persian, III. 113*b*  
**Redruthite**, II. 517*d*  
**Red**, Sensitol, III. 516*c*  
 — silver ore, I. 439*d*  
 —, Solway Rubinol, R, I. 400*d*  
 —, stringy-bark, IV. 391*a*



- Red**, Toluylene, I. 569a  
 —, Turkey, calico printing, I. 203c; IV. 181c, 184d  
**Reductase**, V. 23c  
**Red**, Victoria, III. 113b  
 —, Violet, Caledon, 2RN, RRN, I. 417b, d  
 —, ware, VI. 8b  
 —, Water bark, IV. 335d  
**Reflection**, vitamin-B, I. 584d  
**Reformatsky reaction**, II. 300b  
**Refraction** and dispersion formulae, V. 540a, 607d  
**Refractive index** of gases, II. 687b  
**Refractories**, catalytic action on methane, II. 319d  
**Refractory**, carbomundum as, II. 360c  
**Refrax**, II. 361a  
**Refrigerant**, carbon dioxide as, II. 326c  
**Refrigerants**, II. 173b  
 "Regipyrin," I. 517d  
**Regulus** (copper), *see* Matte  
 — of Venus (antimony), I. 416a  
**Reichardtite**, IV. 321b  
**Reichert-Meißel** value of butter, II. 165a  
 — — — — — cacao butter, II. 185b  
**Reinecke's salt**, III. 115b  
**Reinsch test**, I. 471b  
**Reiss test**, IV. 517d  
 "Renalina" I. 147d  
**Rennet precipitation**, II. 113a, 525d  
**Rennin**, IV. 315d  
**Reppmann test**, I. 471c  
**Resacetophenone**, II. 158b; VI. 399d  
**Reserve styles** in textile printing, IV. 183d  
**Resin**, Highgate, VI. 220c  
 —, Indian hemp, VI. 422c  
**Resins**, synthetic, acetaldehyde, I. 29a  
 —, —, acetylene derivs., I. 87c  
 —, —, *m*-cresol, III. 427d  
 —, —, fibres, V. 113b, 124d  
 —, —, formaldehyde-phenol, I. 1a; V. 322b  
 —, —, in base-exchange reactions, VI. 218b  
 —, —, lacquers, II. 472d  
 —, —, photographic film, II. 418a  
 —, —, urea-formaldehyde, II. 477b  
 —, —, vinyl derivs., I. 87c, 90c, 93c  
**Resin test**, I. 181a  
**Resist styles** in textile printing, IV. 183d  
**Resonance hybrid**, VI. 257a  
 — of hydrogen, IV. 274c  
**Resorcinol**, antiseptic, IV. 20c  
 —, colour reaction with pentoses, II. 287b  
 —, from brazilin, II. 68d  
 —, —, butin, II. 158a  
 —, —, phenol, II. 307a  
 —, reaction with caramel, II. 277a  
 —, trinitro-, IV. 542b  
 —, —, lead salt, IV. 542c  
**Resorcinylic monoacetate**, IV. 401d  
 **$\beta$ -Resorcyclic acid** from brazilin, II. 69a  
**Respirators**, III. 18b  
 —, charcoal in, II. 320b  
 —, industrial, III. 19d  
**Respiratory ferment**, iron in, II. 422c  
**Retene**, I. 1d, 2b; II. 261b; V. 169d  
 —, hydro-derivs., I. 1d, 2c  
**Retentivity** of charcoal, II. 318a  
**Reticulin**, VI. 21b  
**Retonation** in gaseous explosions, IV. 134d  
**Retort carbon**, V. 153a  
**Retting**, dew, tank, water, and chemical, V. 159d  
 —, of linen, II. 11a  
**Réuniol**, III. 192c; V. 519b  
**Revdanskite**, V. 430a  
**Revertose**, II. 209a  
**Rhamnase**, II. 299d; IV. 314b  
**Rhamnazin**, VI. 94d  
**Rhamnetin**, I. 102a; II. 120c  
**isoRhamnetin**, I. 499a; III. 200a  
**Rhamnucoside**, VI. 94d  
**Rhamnucosin**, sugar in, II. 300b  
**Rhamnose**, II. 301b  
**Rhamnocathartin**, II. 120c  
**Rhamnol**, II. 411a  
**Rhamnose** in cardiac glycosides, II. 381c  
*l*-**Rhamnose**, II. 287c  
**Rhamnosides** in *Cascara sagrada*, II. 410d  
**Rhamnoxanthol**, II. 120c  
**Rhamnus alaternus**, *R. infernalis*, *R. japonica*, I. 559d, 560a; VI. 90c, 98a  
 — *catharticus*, III. 556b; VI. 94d  
 — *frangula*, I. 108a; V. 328d; VI. 88a  
**Rhatanine**, I. 371d; V. 517a  
**Rhea** (*see also* Rame), III. 31; V. 163c  
**Rhein**, I. 225d  
**Rhenium**, detn., gravimetric, II. 610d  
 —, —, volumetric, II. 605d  
 —, qualitative reactions, II. 554d, 559b, 577d  
**Rheonine**, I. 133b  
**Rheopexy**, III. 292a  
**Rheum emodi**, eugenol from, IV. 394d  
**Rhinanthin**, I. 517c  
**Rhizocaline**, VI. 138c  
**Rhizopus spp.** in fermentations, V. 50b, 51a  
**Rhodallin**, I. 259b  
**Rhodamic acid**, I. 319b  
**Rhodeose**, rhoditol, II. 287c; V. 330c  
 "Rhodiaseta" rayon, I. 39c  
**Rhodinal**, III. 191c  
**Rhodine**, III. 77a  
**Rhodinol**, III. 192c; V. 519b  
**Rhodites rosa**, V. 426c  
**Rhodium**, detn., electrodeposition, II. 702a  
 —, —, gravimetric, II. 614c  
 —, electrodeposition, IV. 269b  
 —, qualitative reactions, II. 554d, 556d, 560c, 578c  
**Rhodizite**, I. 264d, 685b  
**Rhodolite**, II. 480b  
**Rhodolite**, V. 429c  
**Rhodophane**, II. 480b  
**Rhodophycæ**, I. 200b  
**Rhodoporphyrin**, III. 82d  
**Rhodoviolascin**, II. 401d  
**Rhodoxanthin**, II. 401a  
**Rhodymenia palmata**, I. 190b, 200c; VI. 88a  
**Rhus colinus**, *R. spp.*, VI. 88b, 92b  
 — *glabra*, *R. semialata*, V. 426c; VI. 90d  
**Ribes grossularia**, *R. spp.*, III. 461c; VI. 124d  
 — *sanguineum*, I. 440a  
**d-Ribodeseose**, in nucleic acids, II. 288b  
**Ribose** in carmine, II. 301a  
**d-Ribose**, II. 287b  
**Rice**, II. 489c  
 —, hulling, II. 490c  
 —, silver husk, s. skin, II. 503c  
**Ricin**, II. 420b  
**Ricinine**, II. 420b  
**Ricinoleic acid**, glycerides, II. 421a  
 — in ergot, IV. 331c  
**Ricinus communis**, IV. 87a  
**Rideal-Walker** coefficient, IV. 32a  
**Riebeckite**, I. 499d  
**Rifle sampler**, I. 518d  
**Rifleite**, IV. 530a  
**Rigan colours**, IV. 234a  
**Rigmel process**, V. 103d  
**Ring** frame spinning, V. 150b  
**Rionite**, IV. 590d  
**Ripeness** of dough, II. 75b  
**Ritter-Kellner pulp**, II. 461d  
 "Rivarol," I. 134a  
**Robinia pseudacacia**, I. 11c, 12b; III. 556a; VI. 94d, 96c  
**Robinin**, III. 556c; VI. 94d  
**Robinoside**, II. 301b  
**Robinoside**, VI. 94d  
**Robison ester**, V. 22a  
**Rocella**, III. 450a  
**Rochette process**, I. 268b  
**Rock analysis**, alkalis in, II. 585c  
 "Rockingham" pottery, VI. 8b  
**Rock-salt**, I. 506d; VI. 173b  
 — — — in experiments on radiant heat, VI. 173c  
 "Rodiaseta," *see* "Rhodiaseta."  
**Roairant** suction machine for glassware, V. 587  
**Romanite**, I. 302d  
 "Rongalite C," V. 320c  
 "Rongalite special," I. 575d  
**Root crops**, III. 432a  
 — knot, V. 139a  
**Rosa** grass oil, V. 517a  
**Rose** Bengale, IV. 316c  
 — geranium oil, V. 519a  
**Roseol**, III. 192c  
**Rose-ore**, V. 519c  
**Rose's metal**, I. 608c  
**Rosin**, I. 3c; III. 294b  
 — in lacquers, II. 469d  
**Rosinduline**, I. 570b  
**isoRosinduline**, I. 575d  
**Rosolane**, I. 577c  
**Rosterite**, I. 684c  
**Rotenone**, III. 559b  
**Rotherham test**, IV. 553d, 555a  
**Rot sleeping** in cotton bleaching, II. 5b  
**Rough flambé**, VI. 12b

**Roumanite**, I. 302*d*  
**RR alloys**, I. 252*b*, 277*a*  
**Rubane**, III. 140*a*  
**Rubanol**, III. 140*c*  
**Rubانون**, III. 140*b*  
**Rubatoxane**, III. 140*a*  
**Rubatoxanone**, III. 140*b*  
**Rubber**, carbon disulphide solvent, II. 342*c*  
 —, carbon in, II. 313*a*  
 —, colouring, II. 194*b*  
 —, electrodeposition, IV. 272*d*  
 —, in casein agglomerates, II. 415*b*  
 — latex, IV. 301*c*  
 — seed oil, IV. 86*c*  
 — substitutes (*see also* Chloroprene, Dunrene, Sovoprene), I. 93*c*  
 — —, use of candlenut oil in, II. 263*a*  
 —, synthetic, I. 30*b*; II. 153*d*  
**Ruberythric acid**, V. 416*c*; VI. 04*d*  
 — — in chay root, II. 523*d*  
**Rubiadin**, V. 415*d*  
 — primeveroside, V. 416*c*  
**Rubia tinctorum**, *R. spp.*, II. 233*b*; VI. 415*c*  
**Rubichloric acid** in chay root, II. 523*d*  
**Rubidium** as trace element, I. 510*a*  
 —, detn., gravimetric, II. 585*a*  
 — in carnallite, II. 390*a*  
 —, qualitative reactions, II. 556*c*, 564*a*, 566*a*  
**Rubies**, artificial, III. 390*b*; V. 511*d*  
 —, imitation, V. 513*d*  
 —, reconstructed, V. 511*d*  
**Rubijervine**, VI. 200*c*  
**Rubinic acid**, II. 438*b*  
**Rubin number**, III. 287*c*  
**Rubixanthin**, II. 390*c*  
**Rubrescerine**, II. 199*b*  
**Rubrobrassicin**, II. 183*b*  
**Rubrocyanine**, III. 517*c*  
**Rubus fruticosus**, II. 1*a*, 119*a*  
**Ruby**, I. 246*c*; III. 398*d*  
 —, chromium in, III. 96*b*  
**Rubyl chloride**, III. 140*c*  
**"Ruby, Oriental,"** V. 513*d*  
**"Ruby, Siberian,"** V. 513*d*  
**Ruddle**, VI. 161*a*  
**Rudge tube** in bleaching powder production, III. 62*a*  
**Rufante acid**, I. 457*c*  
**Rufi-condensation**, I. 400*d*  
**Rufigallic acid**, *see* Rufigallol.  
**Rufigallol**, I. 213*a*, 227*c*  
**Ruffopin**, I. 213*a*, 226*b*  
**Rumantit**, I. 302*d*  
**Rumppfi acid**, I. 658*c*  
**Rust**, black, V. 130*a*  
**Rusting of iron**, III. 371*b*, 382*a*, 393*b*  
**Rutacarpine**, IV. 415*c*  
**Ruthenium carbonyl**, II. 357*a*  
 —, detn., II. 613*c*  
 —, qualitative reactions, II. 554*d*, 556*d*, 578*b*  
**Rutile**, I. 370*a*; II. 393*b*; IV. 279*d*  
**Rutin**, VI. 95*a*, 98*a*  
 —, sugar in, II. 300*c*  
**Rutinose**, II. 298*b*, 300*c*; III. 549*d*  
**"Rutonal,"** I. 623*a*

## S

**Sabanejev's base**, I. 101*b*  
**Sabaphosphines G, GG**, I. 132*d*  
**Sabatier and Senderen's process**, VI. 177*d*  
**Sabinene** in cardamoms, II. 381*a*  
**Sabinol**, carvenol from, II. 404*d*  
**Sabulite**, IV. 404*b*, 556*a*  
**Saccharic acid**, II. 285*c*, 298*a*  
**Saccharin**, antiseptic action, IV. 28*d*  
**Saccharomyces cerevisiae**, II. 97*a*  
 — *ellipsoides* for glycerin production, VI. 41*c*  
 — *spp.*, effect on fusel oil composition, V. 407*c*  
 — *theobroma*, III. 231*c*  
**Safflower oil**, IV. 86*b*  
**Saffron**, components, III. 428*c*  
**Safranine**, I. 570*b*  
 — *R. T.*, I. 573*b*, 576*d*  
**Safranols**, *apo-* and *iso-*, I. 564*a*  
**Safranols**, I. 570*c*  
**Safranine**, I. 571*a*  
**Satrole** in camphor oil, II. 240*b*  
**Sagakuchi reaction**, VI. 140*b*  
**Sail cloth**, V. 195*d*  
**St. Gobain method**, V. 76*b*  
**St. Helen's Powder**, I. 326*c*  
 — "St. John's bread," I. 658*d*  
**Saké fermentation**, V. 50*b*  
**Sakuranin**, VI. 95*a*  
 — "Salacetol," I. 517*d*  
**Salad oil**, IV. 252*c*  
**Sal ammoniac**, I. 351*d*  
 — "Salaspin," I. 517*d*  
 — "Salbromin," II. 118*b*  
 — "Salcetin," I. 517*d*  
**Salap-mannan**, II. 302*d*  
**Salicin**, VI. 95*a*  
**Salicinerin**, VI. 93*c*  
**Salicylaldehyde** in cassia oil, II. 418*d*  
 —, oxidation, II. 430*c*  
**Salicylaldoxime**, II. 586*b*  
**Salicylates**, qualitative reactions, II. 570*b*  
**Salicylic acid**, acetyl-, I. 119*d*, 517*d*  
 — —, calcium salt, I. 370*a*, 517*d*  
 — —, antiseptic, IV. 28*d*  
 — —, formation, II. 364*b*  
 — —, from phenol, II. 307*a*  
 — — in butter, II. 168*a*  
 — —, food, detection and detn., V. 303*c*  
 — —,  $\alpha$ -naphthyl ester, I. 202*d*  
 — —, production, II. 326*a*  
 — —, salicoyl-, IV. 16*c*  
 — —, synthesis, II. 364*b*  
**Salinigrin**, VI. 93*c*  
**Salinreposeid**, VI. 95*b*  
**Salix cinerea**, *S. helix*, VI. 93*d*, 95*a*  
**Salmenic acid**, I. 532*c*  
 — "Salmester," IV. 333*b*  
**Salmine**, I. 450*c*  
**Salmon oil**, V. 220*a*  
**Salol**, II. 307*b*; IV. 20*a*  
 — "Salophen," II. 516*d*; IV. 29*a*  
**Sal sedativum**, II. 34*d*  
**Salsola kali**, *S. soda*, II. 3*a*; I. 630*d*  
**Salsolino**, methylation, II. 390*d*

**Salt as preservative**, V. 302*c*  
**Saltcake** for glassmaking, V. 560*c*  
**Salt dyes**, IV. 127*a*  
 — effect in catalysed reactions, VI. 243*b*  
 — —, primary and secondary, VI. 246*b*, 247*a*, 394*d*, 396*d*  
**Salting out**, III. 286*b*  
**Saltpetre**, II. 2*d*  
 — "Saltpetre rot," II. 222*c*  
**Salts**, effect on concrete, II. 148*b*  
 — "Salufer" disinfectant, IV. 22*d*  
 — "Salvarsan 606" I. 468*c*, 480*b*, 491*b*  
*Salvia hispanica*, *S. patens*, *S. splendens*, IV. 86*b*; III. 553*d*; VI. 92*a*  
**Salvinian**, VI. 92*a*  
**Sal-volatile**, I. 351*c*  
**Samarium**, II. 511*f*  
**Samariskite**, II. 511*d*; IV. 245*c*, 321*c*  
**Sambucicyanin**, IV. 260*a*  
**Sambucina**, IV. 260*d*; VI. 95*b*  
**Sambucine**, IV. 260*b*  
*Sambucus nigra*, *S. spp.*, VI. 95*b*; IV. 259*d*  
**Sambunigrin**, I. 358*a*; IV. 260*b*; VI. 95*b*  
**Samiresite**, I. 685*c*  
**Samite**, I. 4*a*  
**Sammethblende**, VI. 101*a*  
**Sammeterz**, VI. 101*a*  
**Samna**, II. 108*c*  
**Sampling for analysis**, I. 518*b*; II. 541*d*  
**Samsomite**, IV. 554*c*  
**Samsu**, II. 496*a*  
**Sanchez - Vello glass tube drawing machine**, V. 589*d*, 591*a*  
**Sandalwood oil**, II. 188*d*  
**Sand and other silicious matter**, determination, IV. 603*c*  
**Sandarac** in lacquers, II. 469*a*  
 — resin, II. 234*d*  
**Sandbergerite**, IV. 590*d*  
**Sand-blast**, I. 4*c*  
 — bomb test, IV. 548*d*  
**Sander's extractor**, IV. 583*a*  
**Sanderswood**, II. 234*b*, 260*c*  
**Sand for glassmaking**, V. 558*c*  
 — lime bricks, II. 148*d*  
**Sandmeyer reaction**, II. 370*a*; III. 585*b*  
 — "Sandoptal," I. 623*a*  
**Sand-paper**, I. 4*b*  
**Sandstone**, I. 4*b*; II. 137*d*  
 —, building, II. 137*c*  
 —, flexible, II. 138*a*  
**Sanforising**, V. 193*c*  
**Sanfourche method**, V. 76*b*  
**Sang de Boeuf**, VI. 12*b*  
**Sanguinaria**, tincture, II. 529*d*  
**Sanguinarine**, II. 527*d*  
 — "Sanitas" disinfectant, IV. 31*b*  
 — "Sanocrysin," VI. 117*d*, 119*a*  
 — "Sanoscent" disinfectant, IV. 31*a*  
*Sansevieria spp.*, V. 168*b*  
**Santal**, I. 650*c*  
**Santalal** in sanderswood, II. 234*d*  
**isoSantalal**, acetyl-, II. 260*d*  
 — in camwood, II. 260*c*  
**Santalal**, I. 466*a*  
**Santalone**, I. 650*d*  
**Santalyl carbonate**, II. 19*a*

- Santene formation**, II. 240c  
**Santol**, I. 650d  
**Santonin**, 7-hydroxy-, I. 497a  
**Saponalbin**, VI. 89b  
**Saponaria aff.**, VI. 95c  
**Saponarin**, VI. 95c  
**Saponin**, calendula, II. 234b  
 —, sapindus, VI. 95b  
**Saponins**, VI. 83c  
 — in digitalis, II. 384a  
 — — mineral waters, I. 158a  
 — — saccharides in, II. 301b  
**Sapotaceæ**, seed oils, I. 655a  
**Sapotalin**, I. 100c  
**Sappan**, II. 195b  
 — liquor, II. 74c  
 — wood, II. 68a  
**Sapphire**, I. 264c; III. 398d  
**Sapphires**, artificial, V. 512d  
**Sapphire**, white, V. 512c, 514a, 520b  
**Sapucaia** nuts, II. 67d. foot-note  
**Sarawak Illipé** nuts, II. 32a  
**Sard**, II. 517b  
**Sardine** oil, V. 227d  
**Sarmentocymarin**, II. 386b; VI. 95c  
**Sarmentogenin**, II. 386b  
**Sarmentose**, II. 381d, 386b; III. 538b  
**Sarsaparilla** root, VI. 86c  
**Sarsapogenin** (parigenin), VI. 95c  
**Sarsaponin**, VI. 95c  
 — "*Sasahite*" bulb, V. 251c  
**Sassolite**, II. 55b; V. 60b  
 — "*Satinite*", VI. 160c  
**Satin-spar**, II. 232b; VI. 150c  
**Saturation** coefficient of  
 — masonry, II. 138c  
**Sauerkraut**, II. 183c  
**Saugschiefer**, III. 579d  
**Saveall** of vacuum pans, IV. 406b  
**Savoy** cabbage, II. 182d  
**Sawarri** lat, II. 168d  
**Saxonia** sporting powder, IV. 519b  
**Saxonite**, IV. 553c  
**Scammonia**, VI. 90c  
**Scammonin**, VI. 90c  
**Scamnosse**, II. 301b  
**Scandia**, II. 480b  
**Scandium**, II. 511c  
 —, detn., gravimetric, II. 594b  
 —, qualitative reactions, II. 585b, 560b, 562b, 568c  
**Scarlet**, Acridine, J, I. 132d  
 —, —, R, 2R, 3R, I. 132b  
 —, Algal, and Algal Scarlet G, I. 232d, 416b  
 —, Azine, I. 577a  
 —, Biehrich, R., Medicinal, I. 688b  
 —, Chrome, III. 113c  
 —, Grelanone, I. 415c  
 —, Indanthrene, 2G, I. 427d  
 —, Induline, I. 574a, 575d  
 — Red, I. 688b  
**Scatole** in civet, III. 104b  
**Schachert's** extractor, IV. 586b  
**Schäffer** acid, IV. 209d  
**Schappe** silk, IV. 124a  
**Schardinger** enzyme, III. 553b  
**Scheelite**, II. 509c; V. 173a  
**Scheiber's** oil, see Synouryn.  
**Scheibler's** extractor, IV. 579c, 580c  
 — lamp, IV. 27b  
**Schiff's** bases, VI. 415b  
**Schlimose**, explosive, IV. 476d  
**Schlempe** cyanide process, III. 464b  
**Schlieren** photography, IV. 433b  
**Schlippe's** salt, I. 446c, 447a  
**Schlossing - Schulze - Tie-mann**, nitrate detn., II. 688d  
**Schnapps**, V. 532b  
 — "*Schneiderite*", IV. 474d  
**Schoepite**, I. 601b  
**Schotten-Baumann** reaction, II. 372c  
**Schou's** oil, IV. 285c  
**Schreiner**, V. 188c  
**Schuckert** cell, III. 65d  
**Schultze** smokeless powder, IV. 517d  
 — sporting powder, IV. 519b  
**Schulze** and von Rampach's extractor, IV. 578a  
**Schwartz** oven, II. 311b  
**Schwarz** extractor, IV. 585c  
**Schwazite**, IV. 590d  
**Schweifelspiessglanz**, I. 440b  
**Schweizer's** reagent, II. 463b; III. 355a  
**Scillabiose**, II. 381d, 387a  
**α-Scillanic** acid, II. 383a  
**Scillaren**, II. 387a; VI. 95c  
**Scillarenase**, II. 387a  
**Scillaridin A**, II. 382a, 383a  
**Sclererythrin**, IV. 332c  
**Sclerocrystallin**, IV. 332d  
**Scombrine**, I. 459c  
**α-Scopalamine** hydrobromide, IV. 405a  
**Scopolin**, III. 120b  
**Scopolin**, I. 100c; III. 413a  
 — VI. 95c  
**Scorodose**, V. 420b  
**Scotch** pebbles, I. 164c  
**Scour** in cotton bleaching, II. 3d  
**Scouring** of loose-wool, II. 12c  
**Scurf** or retort carbon, V. 453a  
 — "*Scuroform*", I. 309b  
**Scutching** of linen, II. 11a  
 — — textiles, II. 461c  
**Scutellareinidine**, II. 275d  
**Scutellaria spp.**, I. 585d; VI. 95d  
**Scutellarin**, VI. 95d  
**Scyllitol**, III. 244b; VI. 405d  
**Scythe-stones**, I. 4c  
**S.D.O.** (synthetic drying oil), I. 90b; IV. 81d, 87b  
**Seailles** process, I. 268b  
**Secale cereale**, *S. cornutum*, IV. 326d  
**Secaleminosulphonic** acid, IV. 332c  
**Secretin**, VI. 268c  
**Sedanoid**, II. 441c  
**Sedanonic** acid, II. 441c  
**Sedimentation**, III. 290a  
 — of starch, II. 302b  
 — potential, III. 283d  
**Sedochetose**, II. 286d  
**Seed** extraction by trichloroethylene, I. 103b  
**Seek** oil, VI. 135c  
**Seeth** water, VI. 430b  
**Sehta**, III. 222c  
**Selacholeic** acid, III. 247b  
**Seladonite**, VI. 136a  
**Selenacyanines**, selenacarbocyanines, seleno-2'-cyanines and seleno-4'-cyanines, III. 520c  
**Selenates**, qualitative reactions, II. 575a  
**Selenazolinocarbocyanines**, III. 522a  
**Selenides**, qualitative reactions, II. 575a  
**Selenious** acid, detn., volumetric, II. 665d  
**Selenite**, II. 232b; VI. 159c  
**Selenites**, qualitative reactions, II. 575a  
**Selenium** as trace element, I. 510b  
 —, detn., gravimetric, II. 603d  
 —, —, micro-method, II. 632d  
 —, elemental, detn., volumetric, II. 666a  
 —, —, identification, II. 575a  
 — in pigment manufacture, II. 104b  
 —, qualitative reactions, II. 554a, 556d  
**Selinene** from eudesmol, IV. 393a  
 — in celery oil, II. 411c  
**Selinol**, IV. 393a  
**Seltzer** water, I. 156a  
 — "*Selvadin*", II. 432d  
**Semicarbazide**, VI. 290b  
**Semicarbazones**, I. 195c; VI. 290c  
**Semi-β-carotenone**, II. 395b, 399b  
**Semi-coke**, V. 364d  
 — — for water-gas production, V. 501b  
**Semidine** rearrangement, IV. 11b  
**Semioxamazine**, VI. 300b  
**Sempervine** and sempervirine, V. 510c  
**Senarmontite**, I. 439d, 440a  
**Sensibamine**, IV. 327d  
**Sensitisation** of sols, III. 287a  
 — "*Sensitol*" colours, III. 515b  
 — "*Senso*", II. 388b  
**Separation** by crystallization, III. 447d  
**Septacrol**, I. 134a  
**Septanose** sugars, II. 282d  
**Septentrionaline**, I. 123c  
**Sequoyitol**, II. 32c  
 — "*Seraceta*", I. 39c  
**Sericin**, V. 86b, 87d  
 — in silk gum, II. 17b  
**Serocrin**, VI. 95d  
**Serpentine**, I. 490c  
 — asbestos, I. 499c  
 — building stone, II. 138a  
 —, chromium in, III. 96b  
**Serum**, antivenom, II. 24d  
 —, blood, proteins, II. 10c  
 — therapy, II. 22a  
**Sesame** oil, brominated, II. 118b  
 — —, German, II. 237a  
**Sesquiterpenes** in cascarrilla oil, II. 411a  
**Setacyl** dyes, I. 42a  
 — "*Setoxyl*", I. 147d; VI. 226a, 354a  
 — "*Sexton*", "*Sextone*", I. 390d  
 — VI. 354a  
 — "*Shaddock*", VI. 129b  
**Shale** from clay, I. 291c  
 — oil, V. 379a

- Shale** oil, carcinogenic action, II. 378b  
 --, gaseous fuels from, II. 3b  
 --, in candle manufacture, II. 263c  
**Shattuckite**, IV. 7d  
**Shea**, butter, I. 654b; II. 168d  
 -- fat in chocolate, III. 88b  
 -- nut oil, I. 654c  
**Shekanin**, VI. 90d  
**Shellac** in lacquers, II. 469a  
 -- storage of pinene, II. 250a  
 "Sherardizing," V. 427b  
**Shikonin**, I. 238a  
**Ship's** nails, I. 445d  
**Shoddy** fertilisers, V. 66c  
**Shogaol**, V. 535a  
*Shorea* spp., nut oils, II. 31c; III. 540d  
**Shortenings**, IV. 253b  
 -- or hard substitutes, III. 410c  
**Shot-dort**, III. 574d  
**Showerproof** fabrics, V. 196d  
**Siak** Illipé nuts, II. 32a  
 "Sichlor," III. 62d  
 "Sicoid," II. 480b  
**Siderite**, II. 519c  
**Siderose**, II. 519d  
**Siemens-Billiter** electrolytic cell, III. 51b  
**Silage**, IV. 308b  
 "Silfrax," II. 361b  
**Silica**, detn., I. 531b; II. 591d  
 --, --, colorimetric, II. 671b  
 --, --, in clay, III. 201a  
 --, drop reaction, II. 582b  
 --, gel, adsorption of carbon disulphide on, II. 310b  
 --, for refining benzol, III. 267d  
 --, native, I. 4b; II. 517b  
 --, qualitative reactions, II. 548c, 570d  
 "Silica skeleton" test, II. 518c  
**Silicates** (see also Clay; Feldspar; individual silicates; Silica), I. 261c, 291b  
 -- in casein paints, II. 415c  
**Silica** ware, V. 600a  
**Siliceous** sinter, V. 530b  
**Silicide**, chromium, III. 109a  
**Silicides**, prepn., II. 360c  
**Silicofluorides**, V. 282c  
 --, qualitative reactions, II. 571a  
**Silicon** borides, II. 45b  
 -- carbide (see also Abrasives; Carborundum), II. 280d, 310b  
 --, detn., see Silica  
 -- in plants, I. 510b  
**Silicenes**, formation, II. 227c  
**Silicon** hydride, II. 227b; VI. 305a  
**Silk**, V. 86a  
 --, artificial, see Cellulose; Cellulose acetate; Fibres, artificial or rayon; Rayon.  
 -- bleaching (wool process), IV. 124b, 139b, 144a  
 -- degumming, V. 94b  
 -- detn., in mixed fibres, V. 95b  
 -- dyeing, IV. 143d; V. 95b  
 -- Eria, V. 80a  
 --, microscopy, V. 91d  
 "Silkool," V. 115d  
**Silk** printing, IV. 187a  
 --, properties, IV. 123d  
 --, raw, composition, II. 19b  
**Silk** reeling, V. 93d  
 --, Shantung, V. 86a  
 -- soaking, V. 94b  
 --, souple, II. 18d; IV. 143d  
 --, stoving, II. 18c  
 --, Tussah, V. 86a  
 --, Vandura or Vandura, V. 115d  
 --, vegetable, I. 261b, 501c  
 -- weighing, IV. 124b, 144a; V. 94d  
**Silkworm**, chrysalid oil, composition, II. 26d  
**Sillimanite**, I. 261d; III. 197a; V. 169c  
 "Silmalec," I. 277a  
**Silos**, IV. 308b  
 "Soloxicon," II. 361b  
 "Silumin, silumin  $\gamma$ ," I. 253b, 277c  
 "Silundum," II. 361b  
**Silver**, action in synthesis of methyl alcohol, II. 350b  
 --, antimonial, I. 416b; IV. 16d  
 -- as trace element, I. 510b  
 -- carbide, II. 281b  
 -- catalyst in metal carbonyl prepn., II. 357c  
 -- cyanate, III. 507c  
 -- cyanide, III. 487b  
 --, detn., assay, I. 529a  
 --, --, colorimetric, II. 672c  
 --, --, electrodeposition, II. 702a  
 --, --, gravimetric, II. 586d  
 --, --, potentiometric, II. 706c  
 --, --, spectroscopic, II. 692a  
 --, --, volumetric, II. 666b  
 --, drop reaction, II. 581a, b  
**Silvered** vessel test, IV. 533d  
**Silver**, electrodeposition, IV. 264c  
 -- fulminate (fulminating silver), V. 384b  
 -- halides in photography, II. 450c  
**Silvering** solutions, V. 603c  
**Silver** iodide in photography, II. 235b  
 -- nitrate, disinfectant, IV. 26a  
 --, --, oxidation of aldehydes by, II. 362b  
 --, oxidation - catalyst for methyl alcohol, II. 427c  
 -- oxide in respirators, II. 347a  
 --, qualitative reactions, II. 551a  
 --, --, rare metals present, II. 554b, 556d, 560c  
 --, recovery, in photography, II. 455a  
 "Silver salt," I. 204c, 210b, 216d  
**Silver** wattle, I. 11c  
**Silvestrene** from carene, II. 389a  
**Simetite**, I. 302d  
**Simonyite**, II. 19b  
**Simul**, V. 169b  
**Sinabin**, VI. 96a  
**Sinamine**, I. 258a  
**Sinapic** acid, III. 94a<sup>+</sup>  
**Sinapin**, III. 94a  
*Sinapis nigra*, II. 2d; VI. 96a  
**Singeing** in cotton bleaching, II. 5b  
**Sinigrin**, VI. 96a  
**Sinistrin**, II. 280c  
**Sinomenine**, IV. 52c  
 "Sinomenium acutum," IV. 52c  
**Sinopite**, II. 26c  
 "Sionin," II. 296c  
**Sisal**, I. 165a; II. 461b  
 -- analysis and testing, V. 167b  
 -- and henequen (see also Agave), V. 166a  
 -- tow and waste, V. 166c, 167a  
**Sitostane**, IV. 326a  
**Sitosterol**, I. 201a; III. 88d; IV. 326a  
**Sitosterolin**, VI. 96b  
**Sitosterol** in bran, II. 60c  
 -- calophyllum oil, II. 235b  
**Size**, concentrated, VI. 25b  
 -- for cotton, V. 153b  
**Sizing**, warp, V. 153b  
**Skatole**, VI. 463b  
**Skiagraphy**, see X-Ray contrast media.  
**Skimmetin**, VI. 96b  
**Skimmianine**, *Skimmia* spp., III. 602b; VI. 95d  
**Skimmin**, III. 413a; VI. 95d  
**Skraup's** synthesis, I. 205a  
**Skutterudite**, III. 220c  
**Slag**, basic, V. 67a  
 --, --, analysis, V. 81c  
 -- in cement manufacture, II. 115a  
**Slanutosterol**, III. 30a  
**Slate**, building, II. 137c  
**Slaying** linen, II. 11b  
**Slip** wool, II. 15d  
 "Slip-fibre," I. 409d  
**Slow-combustion** test, V. 219d  
**Smalt**, II. 19a; III. 219c, 220c  
**Smaltite**, I. 469a; III. 34d, 211b, 220c  
**Smaragde**, IV. 270b  
 "Smectite," V. 381d, 382d  
**Smithsonite**, II. 201b; VI. 137a  
**Smokeless** powders (see also Nitro-explosives), IV. 517c  
 --, analysis, IV. 532a  
 --, ballistics, IV. 535b  
 --, colloidal agents, IV. 523c  
 --, erosion, IV. 531d  
 --, ignition-point and residue, IV. 529c  
 --, mode of burning, IV. 529a  
 --, nitro-starch, IV. 528c  
 --, non-rusting, for small arms, IV. 528c  
 --, products of combustion, IV. 529d  
 --, properties, IV. 528d  
 --, sensitiveness to shock, IV. 529c  
 --, stability tests, IV. 530d, 533c  
**Smokes**, respirators for, III. 10d  
**Snakeroot**, black, I. 137a  
**S-N** process, de Laval, I. 103c  
 "Soamin," I. 486d, 547a  
**Soap**, see also Detergents; Dry cleaning; Fats, hydrolysis; Fats, saponification; Glycerin.  
 --, castor oil in, II. 420c  
 --, colouring, II. 194b  
 --, making, VI. 22c  
**Soaps**, soft, candlenut oil in, II. 263a  
**Soapstone**, II. 138a, 518c  
 "Soda acid," I. 48b

- Soda ash** for glassmaking, V. 580c  
 -- Bordeaux, III. 355d  
 -- lime in analysis, II. 616c  
 -- in respirators, III. 10c  
**Sodalite**, I. 204d  
**"Soda nitre"** for glassmaking, V. 500c  
**Sodiocamphor**, II. 242d  
**Sodium acetate** production, II. 233c  
 -- alkyls, reaction with carbon dioxide, II. 363c  
 -- aluminate, I. 284c  
 -- aluminum fluoride, III. 33d  
 -- (and potassium), detn., volumetric, II. 666c  
 -- anthraquinone-2-sulphonate, I. 201c, 210b  
 -- aquopentacyanoferrate, III. 477b  
 -- aquopentacyanoferrate, III. 477b  
 -- arsenate, I. 478d  
 -- arsenite, I. 477c  
 -- aurocyanide, III. 486b  
 -- benzenesulphonate, for hydrolysis of bornyl chloride, II. 252d  
 -- benzoate, antiseptic, preservative, IV. 28c; V. 300c  
 -- bismuthothiosulphate, reagent, II. 553d  
 -- borate in purifying phenol, II. 301d  
 -- borosacchylate, II. 53c  
 -- carbide, II. 280d  
 -- carbonate, production, II. 326a  
 -- carbonyl, II. 357c  
 -- cellulose xanthate, II. 312d  
 -- chemiluminescence, III. 23b  
 -- chlorate, III. 67a  
 -- chromate, III. 111b  
 -- cyanate, III. 507b  
 -- cyanide, III. 481c  
 -- in froth flotation, III. 485c  
 -- gold extraction, III. 486b; VI. 104a  
 --, detn., gravimetric, II. 581a  
 -- in clay, III. 203c  
 --, volumetric, IV. 3b  
 -- diborate, *see* Borax.  
 -- dichromate, III. 111a  
 -- ferrocyanide, III. 475a  
 -- formate from carbon monoxide, II. 350d  
 -- hexametaphosphate, II. 234b  
 -- hydrosulphate (dithionite), IV. 126b  
 -- hypochlorite, III. 61d  
 -- in plants, I. 510b  
 -- magnesium sulphate, II. 19b  
 -- meta-arsenite, I. 477c  
 -- metaborate, II. 51b  
 -- molecular, II. 368a  
 -- morthuate, III. 250c  
 -- nitrate, II. 234b; V. 500c, 501a  
 -- fertiliser, V. 65b  
 -- *p*-nitrobenzenediazo - oxide, III. 597b  
 -- nitroprusside, III. 477a  
 -- "Sodium perborate," II. 51d; VI. 345c  
**Sodium phenate**, hydrolytic agent, II. 252d  
 -- in respirators, III. 18b  
**Sodium propiolate** from acetylene, I. 85a  
 --, qualitative reactions, II. 554c, 556c, 563b, 566a  
 -- salicylate, II. 308d, 361b  
 -- silicate in wool scouring, II. 16a  
 -- stearate, hydrolytic agent, II. 252d  
 -- sulphate for glassmaking, V. 500a  
 -- tetraborate, *see* Borax.  
 -- thiosulphate in respirators, III. 18b  
 -- *p* - toluenesulphonchloroamide, III. 36a  
 -- zirconate, II. 429c  
**Sod oil**, III. 551b, 551d, footnote  
**"Soentat"** fat, II. 32b  
**Soft purple stone**, III. 32c  
**Soja hispida**, I. 659c; IV. 189d; V. 259c; VI. 88c  
 --, allantonases from, I. 240a  
 -- mar, IV. 81c  
**Solanine**, VI. 90b  
**Solanocapsine**, VI. 90b  
**Solanose**, II. 301b  
**Solanum spp.**, III. 551c; IV. 257a; VI. 90b  
**"Soledon"** dyes, I. 120b; IV. 129c; VI. 457a  
**"Solganol B,"** VI. 119a  
**Solid-phase rule**, III. 202b  
 -- solutions, interstitial, VI. 281c  
 --, substitutional, VI. 281c  
**Sols**, hydrophilic, III. 290c  
 --, hydrophobic, coagulation, III. 285b  
 --, isodisperse, III. 289a  
 --, polydisperse, III. 289a  
 --, viscosity, III. 200c  
**"Soluble Alumina,"** I. 290d  
**Soluble anhydride**, II. 139a  
**"Solusalvarsan,"** I. 492c  
**Solvation** and co-ordination theory, VI. 208a  
 -- electronic theory, VI. 208b  
**Solvent**, electrostriction, VI. 297c  
 -- recovery (*see also* Adsorption; Charcoal, active), Daniel and Brégeat process, III. 364a  
**Solvents**, chlorinated, toxicity, I. 105c; II. 356b  
 --, dry cleaning, IV. 57d  
 --, non-inflammable, *see* Carbon tetrachloride; Ethylene trichloro-  
**"Solway"** colours, I. 401c  
**"Soneryl,"** I. 623a  
**Soot**, II. 312a  
 -- fertiliser, V. 66d  
**Sophoricoside**, IV. 180d  
**Sophorin**, VI. 90c  
**Sophorine**, III. 512c  
**Sorbitol**, I. 451c; II. 286c  
 -- from glucose, II. 285b  
**Sorbose**, II. 282b, 286b  
**Sorghum**, II. 482c, 483a  
 --, hydrocyanic acid in, II. 483d  
 **$\alpha$ -Sorinin**, VI. 96c  
**Souari fat**, II. 168d  
**Sour** in cotton bleaching, II. 3d  
**Souring** of clay, III. 190d  
**Sovoprene**, sovprene, I. 80d  
**Sozhlet** and Szombathy's extractor, IV. 581a  
**Soya bean oil**, IV. 84c  
 --, detection, II. 186a  
**Soya hispida**, *see* Soja hispida.  
**Soybean oil**, *see* Soya bean oil.  
**Soy fermentation**, I. 50b  
**Sozoidolic acid**, I. 319b  
**Sparging** in brewing, II. 95a  
**Sparry calamine**, II. 201b  
**Sparteine** in chelidonium, II. 528a  
**Spectrograms**, interpretation, II. 690a  
**Spectroscope**, Hartridge reversion, VI. 166b  
**Spectroscopic detn.** of interatomic distances, VI. 502c  
**Spectrum analysis**, II. 688d  
 --, arc, II. 680a  
 --, flame, II. 680a  
 --, quantitative, II. 687c, 690b  
 --, spark, II. 680b  
**Speise** (speiss), I. 520d  
**Speiss**, III. 214d, 219d  
**Spent oxide**, cyanogen compounds from, III. 407d, 508a  
**Spermaceti** in candles, III. 203b  
**Spermatolipase**, II. 420b  
**Spermine**, I. 315b  
**Speryllite**, III. 327c, 413d  
**Spessartine**, V. 420b  
**Sphaerosiderite**, II. 519d  
**Sphene**, I. 450b; II. 229d  
**Sphingosine** in cerebrosides, II. 506d  
**Spices** as preservatives, V. 207a  
**Spiculisporic acid** from moulds, V. 52d  
**Spießganzweinstein**, I. 118b  
**Spinasterolin**, VI. 96c  
**Spindle tree**, IV. 400c  
**Spinel**, I. 201c  
 --, gem, V. 512d, 513d  
**Spinels**, I. 284c  
**Spinnerets** for rayon, V. 110d, 110b, 123c  
**Spinning drafts**, V. 149b  
**"Spinocaine,"** I. 360d  
**Spinulosin**, V. 54a  
**Spiraea spp.**, VI. 90a, 92a  
**Spirain**, VI. 90a  
 -- "Spirarsyl," I. 401b  
**"Spirit Acid,"** I. 44b  
**"Spirit indication"** of beer, II. 104c  
**Spirits** of hartshorn, I. 327d  
 -- of salt, III. 60b  
**Spiritus aetheris nitrosi**, IV. 365c  
 -- *Vini Gallici*, II. 62d  
 -- "Spirocide," I. 489c  
**Spiro-5:5-dihydantoin**, VI. 289d  
**Spirographisæmin**, VI. 168c  
**Splint** (coal), V. 347b  
**Spodumene**, I. 264d  
 -- as gem, V. 513d  
**Spondias tutea** I. 560d  
**Spon yeast**, II. 78d  
**"Spote starch,"** V. 57d  
**Spyrogelite**, I. 656d

- Sporting powder**, IV. 450b, 519a  
 —, smokeless, IV. 528a  
**Spot tests**, *see* Drop reactions.  
**Spray evaporation**, IV. 414c  
**Spreading coefficient**, VI. 510b  
**Sprengel explosives**, IV. 545b  
**Sprengelpeter**, IV. 404a  
**Sprintillamine**, VI. 200b  
**Sprintilline**, VI. 200b  
**Sprits** in bleached linen, II. 12a  
**Spurrite**, I. 102b  
**Squill**, II. 381b, d, 386d  
**S.R.A.** acetate silk dyes, I. 40d, 41b, 205c  
 " **Stibilarian**," I. 492c  
**Stabilisation** of nitrocellulose, II. 464b; IV. 510c  
**Stabilisers**, IV. 520a  
**Stability tests**, nitro-explosives, IV. 515c, 538c, 547a  
**Stachydrine**, I. 497b, 686c  
**Stachyose**, I. 497b; II. 282b, 301c  
**Stainless steel**, III. 105c, 388b  
**Stand oils**, IV. 88c  
**Stannates**, complexes with catechol, II. 430d  
**Stannic acid**, colloidal, II. 419c  
 — chloride in warfare, III. 10c  
 — production, III. 17a  
 — salts, detn., volumetric, II. 608a  
 —, qualitative reactions (*see also* Tin), II. 571c  
**Stannous salts**, detn., volumetric, II. 607d  
 —, qualitative reactions (*see also* Tin), II. 571b  
**Stantienite**, I. 302d  
**Staphisagrine**, III. 557b  
**Staple fibre**, IV. 125a; V. 113c, 127c  
**Star anise oil**, I. 377a  
 " **Star antimony**," I. 444a  
**Starch** (*see also* Cereals), II. 282a, 457a  
 —, action of diastase on (*see also* Amylase; Diastase; Enzymes), II. 298d  
 — equivalent, IV. 600d  
 —, maintenance, IV. 601a  
 — of feeding stuffs, IV. 597a  
 —, production, IV. 601a  
 —, Floridean, I. 200d  
 —, formula, II. 301c  
 — glycerite, II. 671d  
 — gum, I. 143c  
 —, maize, II. 482a  
 — removal, enzymatic, II. 5b  
 —, rice, II. 494c  
 —, soluble, or solubilised, II. 302c; III. 568a  
**Stassfurtite**, II. 30c  
**Staurokite**, IV. 270d  
**Stavesacre** seeds, alkaloids, III. 557a  
**Steam** as disinfectant, IV. 10d  
 — colours, II. 74c  
**Stearic acid** in bone fat, II. 29b  
 — candles, II. 263c  
 — cascarilla oil, II. 411a  
 — acids, hydroxy-, VI. 405b  
**Stearidonic acid**, III. 247b  
**Stearine** in candles, II. 203c  
 — -rd, II. 264b  
**Stearin**, fish, III. 245c; VI. 135b  
**Stearoptene**, definition, IV. 258a  
 — in attar of roses, I. 547b  
 — citron oil, III. 181a  
**Steatite**, I. 162c; II. 518c  
**Steel analysis**, *see* individual elements.  
 —, carbondum addition to, II. 360c  
**Steels**, alloy, III. 105b, 217c, 388b; VI. 510c  
 " **Stellite** " alloys, III. 217b  
**Stentering** machine and process, V. 185c, 187d  
**Stercobilin**, I. 692a  
**Stereochemistry** of cardiac aglycones, II. 382d  
 — cinchona alkaloids, III. 146c  
 — diazo-compounds, III. 591a  
**Stereoisomerism** of tiglic and angelic acids, II. 177c  
**Stereotype metal**, I. 445d  
**Steric** hindrance in esterification, IV. 340d  
**Sterol** of silkworm, II. 26d  
**Sterols**, cabbage, sterols, rice, II. 183a, 494a  
 — in butter, digitonin test, II. 166d  
 — of cacao butter, II. 185d  
**Stenosing**, V. 129c  
 " **Stibacetrin**," I. 436b  
**Stibacridinic acid**, I. 438a  
**Stibanilic acid**, amino-substituted derivs., I. 436c, d  
 —, nuclear-substituted derivs., I. 436d  
 —, salts, I. 436b  
**Stibinobenzenes**, I. 438c  
**Stibium sulphuratum nigrum**, I. 440b  
**Stibnite**, I. 439d; IV. 591d  
**Stibonic acids**, miscellaneous, I. 437a, b  
**Stiffening fabrics**, V. 186b, 187a  
**Stigmasterol**, II. 494a; VI. 273c  
 " **Stilbosan**," I. 436d  
**Stillinga** tallow, III. 33b  
**Stipites jalapae**, VI. 90c  
 " **Stocko**," I. 703d  
**Stokesite**, I. 457b  
**Stoke's law**, III. 285a  
 — for emulsions, IV. 291a  
**Stone**, blue, II. 25a; III. 357b  
 — dust in coal-dust explosions, IV. 109c, 117a  
 — lime, II. 133c  
 — preservatives, II. 139d  
**Storax**, I. 617a  
 —, cinnamic acid from, III. 180d  
**Storch-Morawski** reaction, III. 205a  
**Storesinol**, I. 617b  
 " **Stovaine**," I. 369a  
 " **Stovarsol**," I. 39c, 480c, 489c  
**Strass**, V. 513b, 605d  
**Stratosphere**, I. 538d  
**Straw**, IV. 505a; V. 61b  
 —, rice, II. 496d  
**Stream** double refraction, III. 289c  
**Streaming** potential, III. 283d  
**Streptococcus spp.**, III. 567c  
**Stretch-spinning** of rayon, V. 116c, 120c, 121d, 123d, 129c, 131c  
**"String"** beans, I. 659a  
**Stringy bark tree**, IV. 391a  
**Stromeyerite**, II. 517d  
**Strontium**, II. 567b  
 —, action on prothrombin, II. 23c  
 — as trace element, I. 510c  
 — detn., gravimetric, II. 589b  
 —, drop reaction, *see* Barium, II. 579d  
 —, qualitative reactions, II. 547c, 553d, 567b  
 —, rare metals present, II. 555d, 556d  
 — sulphate, II. 442b  
**Strophanthidin**, II. 382a, 385b, d, 386a  
**alloStrophanthidin**, II. 385d  
**k-Strophanthin-β**, II. 385b; VI. 96c  
**Strophantobias**, IV. 314b  
**Strophantobiose**, II. 300b, 381d  
**Strophantus spp.**, I. 120d; III. 538b; IV. 87d  
**Strychnine**, carbazole from, II. 278d  
 —, occurrence, II. 182a  
**Strychnos spp.**, III. 459c  
**Stupho** photometer, III. 304d  
**Stupp**, V. 269d  
**Sturine**, I. 459c  
**Stylopine**, III. 359d  
**Styphnic acid**, IV. 542b  
 —, lead salt, IV. 542c  
**Styracin**, I. 617b  
**Styracitol**, II. 295a  
 " **Styracole**," VI. 140d  
**Styrax Benzoin**, *S. spp.*, I. 615a, 617c  
**Styrene** from cinnamic acid, II. 373b  
**Suaveoline**, I. 496d  
**Suberic acid**, III. 366b  
**Suberin**, III. 366a  
**Suberimic acid**, III. 366a  
**Suberolic acid**, III. 366b  
**Suberylarginine**, II. 388b, c  
 " **Sublamine** " antiseptic, IV. 25d  
**Substantive dyes** (*see also* Dyes, direct cotton), IV. 127c  
 —, components and performance, IV. 215c, 224c  
**Substrate**, definition, VI. 395b  
**Succinates**, qualitative reactions, II. 570a  
**Succinic acid** fermentation, V. 43a  
 —, bacterial, V. 50b  
 —, n-heptyl-, VI. 205d  
**Succinite**, I. 301d  
**Succinonitrile** from acetylene, I. 84d  
**Succinyl peroxide**, I. 262d  
 " **Suchar**," I. 153a  
**Sucrase**, IV. 314b  
**Sucrose**, II. 282a, 299d  
 —, colour reaction, II. 300b  
 —, inversion, II. 530d; VI. 244a, 382a  
**Suction gas** (*see also* Producer gas), II. 345a; V. 373d  
 — plant, V. 373b  
**Sudan rv.**, I. 688b  
**Sugar** as preservative, V. 302b  
 — beet, I. 661c  
 —, detn. in chocolate, III. 86d  
 —, in feeding stuffs, IV. 603a  
 —, refining, II. 320a, 442b

- Sugars**, effect on concrete, II. 148b  
 — of cardiac glycosides, II. 381c  
 —, separation, II. 293b  
**Suint**, acetone oil from, I. 71a  
 — in wool scouring, II. 12b, 13d  
**Suketodara** liver-oil, III. 244c  
**Sullivan's** test, VI. 144b  
**Sulochrin**, *V.* 57a  
**Sulphantimonites**, I. 439d;  
 VI. 154d  
**"Sulpharsphenamine"**, I. 492  
**Sulphatase**, IV. 314b  
**Sulphate**, detn., colorimetric, II. 674c  
 —, gravimetric, II. 603c  
 —, volumetric, II. 667a  
**"Sulphate of barytes"**, I. 651a  
**Sulphates**, oxidation of carbon monoxide by, II. 346a  
 —, qualitative reactions, II. 594c, 574d  
**Sulphato** dyes, I. 43a  
**Sulphide**, detn., gravimetric, II. 603a  
 —, potentiometric, II. 700c  
 —, volumetric, II. 666c  
**Sulphides** and hydrogen sulphide, detection, II. 574b, 683d  
**Sulphite** cellulose, II. 232b, 461c  
 —, detn., gravimetric, II. 602b  
 —, volumetric, II. 666d, 685b  
**Sulphites** and sulphurous acid in food (*see* Sulphur dioxide in food), V. 305b  
 —, qualitative reactions, II. 565a, 574c  
**Sulphoacetic** acid, I. 59b  
**Sulphobenzide**, hexanitro-, IV. 481d  
**Sulphocamphylic** acid, II. 248b  
**Sulphocarbonic** acid, II. 328b  
**Sulphocyanides**. *see* Thiocyanates.  
**"Sulphoform"**, I. 435d  
**Sulphonated** oils, IV. 280a  
**Sulphonates**, alkylated aromatic, IV. 280b  
**Sulphones**, plasticisers, II. 448c  
**Sulphonic** acids from petroleum, III. 560c  
 —, production, II. 428d  
**Sulphosil**, II. 506d  
**Sulphur** acids, detn., volumetric, II. 666c  
 — chloride from carbon disulphide, II. 353c  
 — in vulcanisation, II. 343c  
 compounds in town gas, II. 349c  
 —, detn., Carius method, II. 621c  
 —, Eschka's method, II. 603b  
 —, Grote and Krekeler's method, II. 621b  
 — in coal and coke, II. 603b  
 —, hydrogenation analysis, VI. 362c  
 —, ores, I. 531c  
 —, micro-methods, II. 632c  
 — dioxide, bactericide, V. 895b  
 —, carbon disulphide from, II. 338a  
**Sulphur** dioxide, catalytic oxidation, II. 423b  
 —, detection, II. 565a, 574c  
 —, detn. (*see also* Sulphurous acid), II. 685b  
 — from gypsum, II. 233b  
 — fumigation, V. 305a  
 — in food, detection and detn., V. 305b  
 —, reaction with calcium phosphate, II. 225a  
 dyes, IV. 128c  
 —, elemental, detn., II. 603a  
 —, volumetric, II. 667c  
 —, drop reaction, II. 581d  
 —, identification, II. 574a  
**Sulphuretted** hydrogen, *see* Hydrogen sulphide.  
**Sulphuric** acid catalytic production or contact process, *see* Sulphur trioxide, catalytic production.  
 —, detn., *see* Sulphate, detn.  
 — ester salts of long chain fatty acids, IV. 286b  
 — for nitroglycerin production, IV. 492d  
 — solvent in analysis, II. 540c  
**Sulphur** in gunpowder, IV. 455d  
 — hops, II. 92c  
**Sulphurised** oils, IV. 90c  
 — vat colours, I. 423b  
**Sulphurous** acid, *see also* Sulphite; Sulphur dioxide.  
**Sulphur** oxides from town gas, V. 245d  
 — recovery from town gas, II. 319d  
 — thiocyanate, in vulcanisation, II. 343c  
 —, total, detn., in coal gas, II. 685c  
 — trioxide, catalytic production, II. 423b, 535c; III. 17b  
 —, detn., in vapours, II. 685c  
 — in warfare, III. 14d  
**Sulphuryl** chloride, production, II. 428d  
**"Sumacarb"**, I. 153a  
**Suma-resinotannol**, I. 615c  
**Summer** oil, III. 410d  
**Sundtite**, I. 370d  
**Sunstone**, I. 559d; V. 2c, 3a  
**"Super-Alumina"**, I. 289c  
**Super-aromatic** properties, V. 890d  
**Superphosphate**, detn. of soluble phosphate in, V. 80a  
 — of lime, II. 223d  
**Superepolyamides** and superpolymers, V. 125b  
**Supersurface** layer in evaporation, III. 605a  
**"Supracapsulin"**, I. 147d  
**"Supranephrene"**, I. 147d  
**"Suprarenalin"**, I. 147d  
**"Suprarenin"**, I. 145c, 147d  
**Suprasterol**, II. 202c  
**Surface** hardening, oxy-acetylene, I. 110a  
 — tension, III. 282b; V. 263d; VI. 506d  
**Surinamine**, I. 371d; V. 517a  
**Surkhi** cement, II. 145d  
**Surveillance** test, IV. 533d  
**Suture-stones**, III. 573c  
**Swedenborgite**, I. 685a  
**Sweet** potatoes, I. 655d  
**"Sweet** spirit of nitre," IV. 865c  
 — waters," VI. 45b  
**Swissing**, V. 188b  
**Sylvan**, V. 400b  
**Sylvanite**, VI. 102a  
**dl-Sylvestrine**, II. 405a  
**Sylvite**, II. 109b  
**Synadelphite**, I. 241d, 264d  
**Synanthrone**, III. 31a  
**"Syncaïne"**, *see* Procaine  
**Syneresis**, III. 291d  
**Syngonite**, II. 238c  
**"Synouryn"** drying oil, IV. 81d, 87a  
**"Synthalin"**, VI. 81b, 144a  
**Synthesis** gas, V. 503a  
**Synthetic** resin fibres, V. 113b, 124d  
**"Synthol"**, II. 350c, 425c  
**Syringic-acid** glucoside, VI. 90c  
**Syringe**, "Little Algy," IV. 21d  
**Syringim**, VI. 90c  
**Sy** test, IV. 534b

## T

- T.4**, III. 535d  
**Taban** Merah fat, II. 32a  
**Table** oil, IV. 252c  
**Tabular** spar, II. 227c  
**Ta-Cha-Yeh**, V. 511b  
**"Tachiol"** antiseptic, IV. 20a  
**Tachydrite**, II. 212d  
**Tachysterol**, II. 202a; IV. 320d  
**Tagerey-verrey**, II. 419a  
**Tagetes** *potida*, I. 101a; VI. 96d  
**Taifushi** oil, II. 522d  
**"Taka-diastra"**, V. 59c  
**Talc**, II. 518c  
**Talhi**, Tallin, I. 11d  
**Taliani** test, IV. 534c  
**Tall** oil, I. 655d  
**Tallow**, definition, VI. 131d  
 — in cacao butter, II. 187a  
 —, sizing, VI. 135c  
 —, vegetable, prima and secunda, III. 33b  
**Talni** gold, I. 11b  
**Talose**, II. 280a  
**Tamari**, V. 50c  
**Tanacetone** (Thujone), I. 6a  
**Tane-koji**, V. 50b  
**Tanghinin**, II. 387c  
**Tangkallak** fat, IV. 4b  
**Tankage** grease, VI. 135a  
**Tannase**, IV. 314a; V. 425c  
**Tannic** acid, acetyl-, I. 30b  
 —, compound with casein, II. 414d  
 —, qualitative reactions, II. 570c  
**"Tannigen"**, I. 30b  
**Tannin**, Chinese, VI. 96d  
**Tanning** agents, synthetic, II. 308d, 461d  
 — substances from cutch, II. 438b  
**Tannin**, hop, II. 91d  
 —, Turkish, VI. 96d  
**Tanret** reagent, I. 235d  
**Tantulates**, qualitative reactions, II. 555d, 556d, 578d

- Tantalite**, III. 309c  
**Tantalum**, I. 3d  
 — and niobium, separation, II. 602a  
 — carbide, II. 280b  
 —, detn., gravimetric, II. 602  
 — production, II. 511a  
 —, qualitative reactions, II. 555d, 558b, 573d  
**Ta Pel**, V. 330a  
**Taraktogenic acid**, II. 522c  
**Taraxacum officinale**, III. 547a  
**Taraxanthin**, I. 201a; II. 398d  
**Tar**, coke-oven gas, III. 264b  
**Tarnishing of metals**, III. 370b  
 — reactions, VI. 224a  
**Tarnowitzite**, I. 457a  
**Tar oils**, hydrogenation (*see also* Hydrogenation of coal), II. 425d  
**Tarpaulins**, V. 195d  
**Tar**, Stockholm, production, II. 310d  
**Tartar emetic**, I. 439b, 418b  
 — powder, I. 448c  
 — substitute, I. 448c  
**Tartaric acid**, dihydroxy-, IV. 3b  
 — anhydride diacetate, carbon suboxide from, II. 352a  
**Tartarus stibiatus**, I. 448b  
**Tartrates**, qualitative actions, II. 570a  
**Tartazine indicator**, VI. 431b  
**Tartaric acid**, amino-, and derivs., I. 247b, c  
**Tartronylurea**, I. 625a  
**Tar**, wood, production, II. 310d  
**Taurine**, III. 541b  
**Taurocholic acid**, I. 689c  
**Tautolite**, III. 512b  
**Tautomerism**, virtual, of cyanines, III. 510a, 524a  
**Taumer process**, VI. 106c  
**Tchou-ma**, III. 31c  
**Tea**, III. 558b  
 —, Abyssinian, I. 11b  
 —, alkaloïds, II. 197a  
 —, Arabian, I. 11b  
 — catechin, II. 438c  
**Teallite**, II. 538a; V. 328c  
**Tea**, theobromine in, II. 197c  
**Tecomin**, I. 688b  
**Tectoridin**, tectorigenin, V. 259d; VI. 96d  
**Tees powder**, IV. 554c  
**Teglam fat**, II. 32c  
**Teisen furnace**, V. 508a  
**"Tekaol"**, IV. 89d  
**"Telenduron"**, I. 703d  
**Tellurethyl**, IV. 372a  
**Telluric acid**, detn., volumetric, II. 667c  
 — bismuth, II. 32d  
 — silver, VI. 206a  
**Tellurine**, III. 578d  
**Tellurium**, detn., gravimetric, II. 604b  
 —, —, micro-method, II. 632d  
 —, electrodeposition, IV. 269d  
 —, qualitative reactions, II. 554, 556d, 575b  
**Tellurous acid**, detn., volumetric, II. 510c, 667c  
**"Temper"**, I. 472c  
**Temper colours on metals**, III. 868c  
**"Tenacit"**, I. 703d  
**"Tenasco"**, V. 131a  
**Tennantite**, III. 341c; IV. 308a; IV. 590c  
**Tenorite**, III. 341c, 354b  
**Tephrite**, I. 652a  
**Tephrosin**, III. 559c  
**Terbia**, II. 512a  
**Terbium**, II. 511c  
**Terebene antiseptic**, IV. 30d  
**Terebene driers**, IV. 91c  
**Terminthic acid**, III. 34a  
**Terminthic acid**, III. 34a  
**Termintholic acid**, III. 34a  
**Termintholinic acid**, III. 34a  
**Terpenes in buchu**, II. 120a  
**Terpenylic acid**, II. 407a  
 —, hydroxy-, II. 407a  
**1:4-Terpin**, I. 501a  
**Terpin**, cineole from, III. 179b  
 **$\alpha$ -Terpinene**, II. 404c  
**Terpinene formation**, II. 251c  
 — in essential oils, II. 381a; III. 24d  
**Terpineol in essential oils**, II. 26b, 240b, 381a; III. 183c  
 **$\alpha$ -Terpineol**, cineole from, III. 179a  
**Terpinolene formation**, II. 251c  
**"Terra alba"**, VI. 160c  
**Terra Cotta**, II. 128d  
**"Terra japonica"**, II. 433b  
**"Terrana"**, IV. 248c  
**Terra ponderosa salita**, I. 635a  
**Terrein**, V. 53a  
**Testosterone**, I. 371a; VI. 275a, 276a  
**trans-Testosterone**, VI. 275a  
**Tetra-amylose**, III. 509c  
**Tetraboric acid**, II. 47d  
**Tetrabutylammonium iodide**, II. 176d  
**Tetrabutylaldine**, II. 157a  
**Tetracarbocyanines**, III. 528a  
**Tetracene**, IV. 542d  
 —, guanylnitrosoguaninoguanyl-, IV. 542d  
**Tetrachlorethane** (tetrachloroethane), IV. 359c  
**Tetradecane - 1 - carboxylic acid**, 14-hydroxy-, IV. 416d  
**Tetradymite**, II. 32d  
**Tetraethylammonium hydroxide**, IV. 355d  
**Tetraethyldiaminodiphenylmethane**, II. 105b  
**Tetraethylene glycol**, IV. 379b  
 — triamine, IV. 377a  
**Tetraethyltétrazone**, IV. 362c  
**Tetrafluoboric acid**, II. 46c  
**Tetraguaiaquinone**, VI. 141b  
**Tetrahedrite**, III. 341c; IV. 590a  
**Tetrahydrocadalene**, II. 100a  
**Tetrahydrocalamene**, II. 201a  
**Tetrahydrocarbazole**, dehydrogenation, II. 278c  
**Tetrahydrocarveol**, II. 405b  
**Tetrahydrocarvone**, II. 405d  
**Tetrahydrochrysene**, III. 118b  
**Tetrahydrocolumbamine**, II. 235c, d  
**Tetrahydroeucarveol**, IV. 391c  
**Tetrahydroeucarvone**, IV. 391d  
**Tetrahydrofurfuryl alcohol**, VI. 355b  
**Tetrahydroguaiase**, VI. 142c  
**Tetrahydrojatrochizine**, II. 235c  
**Tetrahydronaphthalene**, *see also* Tetralin.  
 —, carcinogenic compounds from, II. 378c  
**Tetrahydroquinaxalines**, I. 316b  
**Tetralin**, (*see also* Tetrahydronaphthalene), VI. 352c  
 — production, II. 426d  
 —, reaction with oxalyl chloride, II. 304a  
**Tetralite**, IV. 485a  
 **$\alpha$ -Tetralone**, VI. 354b  
**Tetramethoxyisoflavylum chloride**, II. 438b  
**1:2:3:5 - Tetramethylbenzene**, II. 242d  
**Tetramethylbenzenes**, III. 539a  
**Tetramethyldistibine** (antimony cacodyl), I. 434c  
**Tetramethylenediamine**, II. 178c  
**Tetramethylenediguanidine**, I. 457a  
**Tetramethyl ferrocyanide**, III. 475b  
**Tetramethylhydric acid**, VI. 407c  
**Tetramethylglucose**, II. 201d  
**Tetramethylphenol**, antiseptic, IV. 7a  
**Tetramethylstibonium hydroxide**, I. 434c  
 — iodide, I. 434c  
**Tetramine reagent for dyes**, IV. 172b  
**Tetrandrine**, VI. 496d  
**Tetraoxymethylene**, V. 320a  
**2:4:5:6-Tetraoxypyrimidine**, I. 243d  
**Tetraphenol**, V. 398b  
**Tetraphenyl methane**, carcinogenic activity, II. 380a  
**Tetrarin**, VI. 97a  
**Tetrasaccharides**, II. 301b  
**Tetrazene**, IV. 542d  
**Tetronic acids from Penicillium spp.**, V. 52b  
**Tetryl**, IV. 485a  
 — chloride, II. 172a  
 —, properties and testing, IV. 486c, 487b  
**Textile emulsions**, IV. 301c  
 printing (*see also* Printing), IV. 175c  
 — by rotogravure, IV. 177c  
 — stencilling, IV. 177a  
 —, colour pastes for, IV. 178c  
 —, crimp effects in, IV. 186a  
 —, discharge styles in, IV. 181d  
 —, engraved rollers for, IV. 176a  
 —, fixing agents for, IV. 178a  
 —, metal powders in, IV. 186b  
 —, pantograph, engraving for, IV. 176b  
 —, pigment lacquer in, IV. 186b  
 —, reserve styles in, IV. 183d



- Textile printing, resist styles**  
 in, IV. 183d  
 — styles, IV. 178d  
 —, thickening agents for, IV. 178a  
 — with hand blocks, IV. 176d  
 — screens, IV. 177a  
 "T-Gas," IV. 380b; V. 395d  
**Thalleioquin, reaction, III.**  
 135d  
**Thallic salts, qualitative reactions, II.** 508c  
**Thallium, isobutyl derivs., II.**  
 173c  
 — copper-silver selenide, III. 430b  
 —, detn., electrochemical, II. 510c  
 —, electrodeposition, II. 702b  
 —, gravimetric, II. 593d  
 —, volumetric, II. 607d  
 — group, qualitative separation, II. 557a  
 — qualitative reactions, II. 547c, 554b, 555d, 560a, 568b, c  
 — salts in carnallite, II. 300a  
**Thallous salts, qualitative reactions, II.** 508b  
 "Thanatol," I. 100d  
*Thea chinensis*, I. 511d  
 — *Sasanqua*, eugenol from, IV. 391c  
*Theobroma cacao*, III. 230d  
**Theobromine, II.** 197a; III. 235c  
 — in cacao butter, II. 186a  
 —, sodio-, sodium iodide addition compound, IV. 405a  
**Theophylline, II.** 197a, d  
 — ethylenediamine, IV. 401a  
**Theosterol, II.** 185d  
**Therapic acid, III.** 247b  
**Therm.** definition, V. 433d  
 "Thermit," "thermite," I. 273b; III. 97b, 103d  
**Thermoluminescence** of fluorspar, II. 215b  
 "Thermolux" glass, V. 595a  
**Thermometer, helium gas, VI.** 199d  
**Thevetigenin, VI.** 97a  
**Thevetin, II.** 380c; VI. 97a  
**Thiacarbocyanines, III.** 517d, 518a  
**Thia-4'-cyanines, III.** 517d  
**Thiacyanines, thia- $\psi$ -cyanines, thia-2'-cyanines, III.** 517d  
**Thiathiazolocyanines, thiazolocarbocyanines and thiazolocyanines, III.** 521b  
**Thiazine, I.** 565a; II. 403d  
**Thiazolinocarbocyanines, thiazolino-2'-cyanines and thiazolino-4'-cyanines, III.** 521d  
**Thieröl, II.** 29d  
**Thiessen furnace, V.** 568a  
**Thioacetones, I.** 69b  
**Thioacridone, I.** 127a  
**Thioarsinites, aryl, I.** 400c  
**Thiobarbituric acid, condensation with aryl aldehydes, I.** 630a  
**Thiocarbonic anhydride, II.** 328b  
**Thiocyanate, detn., potentiometric, II.** 700c  
 —, —, volumetric, II. 655a  
**Thiocyanates, analysis, III.**  
 511d  
 —, prepn. from ammonia and carbon disulphide, III. 507c  
 —, — coal gas, III. 508c  
 —, — cyanamide and sulphur, III. 508a  
 —, — gas liquor, III. 508b  
 —, — spent oxide, III. 508a  
 —, qualitative reactions, II. 509b  
**Thiocyanine, III.** 518a  
**Thiocyanogen value of fats, III.** 509a  
 — values of cacao butter, II. 185b  
**Thiodiethylene glycol, IV.** 381b  
**Thioethylene glycol, IV.** 381a  
 — diacetate and dibenzoate, IV. 381a  
 "Thioform," I. 700c  
**Thioformaldehyde, V.** 320c  
 — formation, II. 312a  
**Thioguaiacol, VI.** 141d  
**Thioguaiacyl xanthate, VI.** 141d  
**Thiohydantoins, VI.** 293c  
**Thiohydrolysis, VI.** 397a  
**Thioindigo and derivs., VI.** 453c  
**Thioindoxyl, VI.** 453c  
**Thioisatins, VI.** 455a  
**Thionaphthenquinones, VI.** 455a  
**Thionates, qualitative reactions, II.** 574c  
**Thionuric acid, I.** 629a  
**Thiophen, colour reaction with isatin, VI.** 403c  
**Thiophenol, by-product, II.** 305a  
**Thiophen, removal from benzole, I.** 674d  
**Thiophosgene production, III.** 17b  
**Thiopropansulphonic acid, sodium auro-salt, I.** 241d  
**Thiosemicarbazide, VI.** 299d  
**Thiosemicarbazones, VI.** 299d  
**Thiosinamine, I.** 259b  
**Thiosulphates, detn., potentiometric, II.** 708b  
 —, —, volumetric, II. 648b, 667b  
 —, qualitative reactions, II. 565a, 574b  
**Thioxanthenes from anthraquinones, I.** 396a  
**Thixotropy, III.** 292a  
**Thomsonite, II.** 229b  
**Thoria catalyst (see also Hydrogenation analysis), II.** 351d, 425d  
**Thorite, II.** 511c  
**Thorium, II.** 511c  
 —, detn., gravimetric, II. 508a  
 —, —, micro-method, II. 633c  
 —, —, volumetric, II. 667d  
 —, qualitative reactions, II. 555b, 556d, 562b, 572a  
**Thortveitite, V.** 524c; VI. 169a  
**Thrombin in blood, II.** 22c  
**Thrombokinase, II.** 23a  
*Thuja occidentalis*, V. 6d  
**Thuja oil, carvotanacetone in, II.** 408b  
**Thujone, I.** 5c, 6a  
 **$\alpha$ -Thujone, rearrangement, II.** 408b  
**Thujyl acetate, I.** 5c  
 — alcohol, I. 5c  
 — palmitate, I. 5c  
 — isovalerate, I. 5c  
**Thulia, II.** 511d  
**Thuringite, II.** 520b  
**Thymidine, VI.** 97a  
**Thymol, di-iodo-, I.** 466b  
 —, reduction, II. 429d  
**Thyroglobulin, VI.** 267b, c  
**Thyronine, VI.** 267d  
**Thyroxine, I.** 506c; VI. 267b  
 —, reactions, VI. 267c  
**Tiemann-Reimer reaction, II.** 304c  
 "Tiers Argent," I. 276a  
**Tiffanyite, III.** 574a  
**Tigers-eye, III.** 430a  
**Tiglic acid, III.** 435a  
**Tigogenin, VI.** 97b  
**Tigonin, VI.** 97a  
**Tile-ore, III.** 450a  
**Tiles, III.** 128a  
*Tilia spp.*, fatty oil, I. 655c  
**Timber-preserving oil, III.** 423d  
**Timonox, I.** 449c  
**Tin, action on phenol, II.** 306d  
 — as trace element, I. 510c  
**Tincal, II.** 30c, 34c, 40d  
**Tin catalysts in hydrogenation, VI.** 308b  
**Tinder-fungus, I.** 298d  
 —, German, I. 298d  
**Tin, detn., assay, I.** 520d  
 —, —, colorimetric, II. 672c  
 —, —, electrodeposition, II. 702c  
 —, —, gravimetric, II. 595d  
 —, — in food, II. 672c; V. 202c  
 —, —, potentiometric, II. 708b  
 —, —, spectroscopic, II. 691c  
 —, —, volumetric, II. 667d  
 —, drop reaction, II. 188c, 581b  
 —, electrodeposition, IV. 269a  
**Ting-yu, III.** 33b  
**Tin oxide, II.** 419b  
**Tinplate, protective lacquers for, III.** 395c; V. 290d, 291b  
**Tin, qualitative reactions, II.** 551c, 571b, c  
 —, —, rare metals present, II. 554c, 556d  
 — stone, II. 419b  
 — white cobalt, *see* Smaltite.  
**Tisu, II.** 157d  
**Titaniferous iron-ore, VI.** 414d  
**Titanite, II.** 220d  
**Titanium as trace element, I.** 510d  
 — carbide, II. 281a  
 — detn., assay, I. 530b  
 —, colorimetric, II. 673a  
 —, gravimetric, II. 596b  
 — in clay, III. 202c  
 — steel, I. 530c  
 —, potentiometric method, II. 708b  
 —, volumetric, II. 668a  
 — drop reaction, II. 581b  
 — oxide, as esterification catalyst, II. 181b  
 —, mineral, II. 119a  
 —, pigment, II. 444b, 475c; V. 128c

- Titanium**, qualitative reactions, II. 571d  
 —, —, rare metals present, II. 555d, 558d  
**Titanomagnetite**, I. 450b  
**Titano-niobates** of rare earths, II. 19b  
**Titanous** chloride, volumetric methods, II. 649a; IV. 239a  
**Titration** errors, VI. 426c  
 — exponent, VI. 426c  
**T.N.A.** (tetranitraniline), IV. 487d  
**T.N.T.** (trinitrotoluene), I. 466c; IV. 466d  
 —  $\alpha$ -,  $\beta$ - and  $\gamma$ -, properties, IV. 471c  
 — as explosive, IV. 472c  
 —, manufacture, continuous process, IV. 468c  
 —, —, intermittent processes, IV. 467b  
 —, physiological effects, IV. 473c  
 —, Queensferry process, IV. 467c  
 — specifications, IV. 471a  
 — testing, IV. 473d  
**Toad** poisons, II. 381b, 387d  
**Toadstone**, III. 571b  
**Tobacco**, III. 558c  
 — smoke as antiseptic, IV. 31b  
 —, —, carbon monoxide in, II. 344b  
**Toddy** wine, I. 467d  
**o-Tolidine**, IV. 12d  
**Tollen's** extractor, IV. 577d  
 — reaction of cardiac glycosides, II. 383d  
**Tolu**, see Balsam.  
**Toluene**, antiseptic, IV. 30d  
**o-Toluene** - azo - o - toluene - azo -  $\beta$ -naphthol, I. 688b  
**Toluene**, chloro-derivs., I. 677d  
 —, dinitro-, IV. 466c  
 — in lacquers, II. 472a  
 —, petroleum, I. 460d  
 —, mononitro-, IV. 460b, 467d  
 —, oxidation to benzaldehyde, I. 678b; II. 428a  
 —, —, benzoic acid, I. 678b; II. 428a  
 —, production, II. 428d  
**Toluenes**, nitro-, I. 676b; IV. 465d  
**p-Toluenesulphanilide**, in lacquers, II. 479a  
**p-Toluenesulphondichloroamide**, III. 36b  
**p-Toluenesulphonyl** compounds of sugars, II. 291b  
**Toluic** acids, hydroxy-, III. 425d  
**m-Toluic** acid from azapin, II. 397a  
**p-Toluidides**, prepn., II. 378a  
**Tolunaphthazines**, I. 566a, 567b  
**Toluphenazine**, I. 567a  
**Tolustilbazine**, I. 568a  
**o-Tolylhydrazine**, I. 197b  
**p-Tolylhydrazine**, I. 197b  
**o-Tolylsemicarbazide**, I. 197a  
**Tonalite**, IV. 7d  
**"Tonite"**, IV. 464b  
**"Tonsil"**, IV. 248c  
**Topaz**, I. 264d  
**"Topaz, Occidental"**, V. 503d  
**Topaz**, oriental, III. 398d  
**"Topaz, scientific"**, V. 512d  
**"Topaz, Spanish"**, V. 513d  
**Topinambur**, topinambour, I. 407a  
**Topped** dyes, IV. 127a  
**Tora**, II. 419b  
**Toringin**, VI. 97b  
**Totaquina**, III. 132b  
**Touchstone** assay, I. 526b  
**Touloucoua** oil, II. 277b  
**Tourils**, III. 75c  
**Tourmaline**, I. 264d, 501a; II. 35b  
 —, gem, V. 513d  
**Tournesol** en drapeaux, I. 688a  
**Tous-les-mois**, I. 468b  
**Townsend** electrolytic cell, III. 53d  
**Toxicarol**, III. 550c  
**Toxol**, I. 301c  
**To-yaku**, V. 516d  
**Tpn**, III. 329c  
**T.P.P.**, I. 263d  
**Trace** elements in plants, see Ash; Boron; Fertiliser, borax, remedial.  
**Tragacanthin**, VI. 156b  
**Train** oil, III. 244d  
**Tram**, V. 94a  
 — silk, IV. 124a  
**Transference** number, VI. 237d  
**Transmutation** of elements, I. 542b  
**Transport** number, VI. 237d  
**Trap-rock**, III. 571b  
**Trash**, V. 146b  
**Trass** in cement, II. 146a  
 —, Rhenish, II. 145d  
**Traumatin**, VI. 138d  
**Trauzl** blocks, I. 355d; IV. 547d  
**Tréfle**, I. 363a  
**Trehalase**, II. 300c  
**Trehalose**, II. 298b, 300c; IV. 331d  
 — monophosphate, II. 296a; V. 21d  
**Tremolite**, I. 490c  
 — asbestos, I. 499d  
**Tren**, III. 329d  
**Trentepohlia** *iolithus*, II. 394a  
**Triacetamide**, I. 60b  
**Triacetin**, I. 60b  
 —, plasticiser, II. 448c, 472c  
 —, specification, II. 472c  
**Triacetanamine**, I. 68d  
 —, nitroso-, catalytic, decomposition, III. 252c  
**Triacetondiamine**, I. 68d  
**Triamyl** citrate, in lacquers, II. 472c  
**Triamylstilbine**, *n*- and *iso*-, I. 434c  
**Triangular** charts, III. 2c  
**Triazidobenzene**, trinitro-, IV. 543a  
**Tribolium confusum**, V. 390b  
**Triboluminescence**, II. 279a; III. 22d  
**Tribromohydrin**, I. 259c  
**Tributylamines**, II. 176c  
**Tributylene**, II. 177d  
**Tributyl phosphine**, II. 176d  
**Tri-3-carbazyl** carbinol formate, II. 279b  
**Tricarbocyanines**, III. 520d  
 —, indo-, seleno-, thia-, thiazolino-, thiazolo-, III. 527b  
**Tricha**, diol, II. 520b  
**Tricresyl** phosphate in dopes and lacquers, II. 448b, 469d, 475d  
 —, —, phenol recovery, II. 305d  
**Tricylene**, elimination from bornylene, II. 93d  
 —, formation, oxidation, II. 254c, 239d  
**Tridentate** groups, III. 329c  
**Trielaidin**, IV. 258d  
**"Trienol"**, IV. 87b  
**Triethanolamine**, I. 307a; IV. 286c, 356a  
 —, absorbent of carbon dioxide, II. 324d  
 — in phenol recovery, II. 305c  
**Triethylamine**, IV. 355c  
 — from acetylene, I. 84c  
**Triethylcarbimide**, IV. 361a  
**Triethylcellulose**, II. 460d  
**Triethylene** chlorohydrin, IV. 379b  
 — glycol, IV. 379b  
**Triethylenediamine**, IV. 376d  
**Triethylenetetramine**, IV. 377a  
**"Triethylenetriamine"**, IV. 377a  
**Triethylhydrazonium** iodide, IV. 362c  
**Triethyloxamine**, IV. 363b  
**Triethyl phosphate**, IV. 366c  
 — phosphite, IV. 366d  
**Triethylpiperazonium** iodide, IV. 376d  
**Triethylstibine**, I. 433c  
**Triethylsulphonium** hydroxide, IV. 370b  
 — iodide, IV. 370b  
**Triethyltelluronium** iodide, IV. 372a  
**Trifolin**, III. 207b  
**Trifolin, isotrifolin**, III. 206d  
**Trifolitin**, III. 206d  
**Trifolium** spp., I. 499b; III. 205c; VI. 90b, 134c  
**Triformal** disinfectant, IV. 26d  
**Trigenic** acid, IV. 382a  
**Trigermane**, V. 522a  
**Trigonella** *Fenum-graecum*, V. 289c  
**Trigonelline** or caffeine, I. 686d; II. 196d; III. 602c  
**Triketohydrindene**, VI. 307b  
 — hydrate, see Ninhydrin.  
**"Trilit"**, IV. 460d  
**Trilobine**, ozonolysis, II. 481b  
**Trimerite**, I. 685a  
**Trimethol**, disinfectant, IV. 29b  
**Trimethoxyglutaric** acid, — from sugars, II. 283b  
**Trimethylacetylhydrazide-ammonium** chloride, V. 536b  
**Trimethylamine** in *Calycanthus occidentalis*, II. 287a  
 — ergot, IV. 331d  
**Trimethylbenzenes**, III. 457a  
**Trimethylallobrazilin**,  $\alpha$ - and  $\beta$ -, II. 72d  
**Trimethylbrazilone**, trimethylbrazilonol, II. 70d, 72c  
**Trimethyl carbinol**, II. 171a  
**Trimethylcellulose**, II. 466c, 477c

- Trimethyl citrate**, III. 186b  
**Trimethylidihydroisobrazil-  
leinol**, II. 72b  
**Trimethylidihydrobrazilone**,  
II. 72b  
**Trimethylene glycol**, VI. 63a  
**cycloTrimethylenimine**, I.  
315a  
**cycloTrimethylenetrinitra-  
mine**, III. 535d  
**Trimethylethylene**, I. 301d  
**d - 2:2:3 - Trimethylcyclo -  
hexan - 4 - one - 1 - car -  
boxylic acid**, II. 247a  
**Trimethylhistidine**, I. 086d;  
VI. 237b  
**Trimethylglucose**, II. 202a  
**Trimethylphenol**, antiseptic,  
IV. 7a  
**Trimethylstibine**, I. 134b  
 -- di-iodide, I. 434a  
 -- oxide, I. 431b  
 -- sulphide, I. 434c  
**1:3:7-Trimethylxanthine**, II.  
197a  
 " **Trinol**," IV. 466d  
**Tri - orthophenanthroline -  
ferrous sulphate**, indi-  
cator, VI. 430d  
**2:4:6-Trioxhexahydropyri-  
midine**, I. 020c  
**Trioxymethylene**, I. 195d  
 **$\alpha$ -Trioxymethylene**, V. 319d  
**Trioxymethylene**, disinsec-  
tant, IV. 26d  
**Triphenylbenzene**, carcino-  
genic activity, II. 380a  
**Triphenylmethyl ethers**, of  
sugars, II. 291a  
**Triphenyl phosphate** in films  
and lacquers, II. 308d,  
448b, 472c  
 --, specification, II. 472c  
 -- urea in lacquers, II. 472c  
**Triphylite**, II. 195c  
 " **Triplastite**," IV. 464c  
**Tripoli** or **Tripolite**, III. 579a;  
IV. 239b  
**Trippy**, III. 329d  
**Trisaccharides**, II. 301b  
**Trisazo benzidine dyes**, IV.  
220b  
**Trithioaldehyde**, II. 177b  
**Triticin**, triticum, I. 171d  
**Triticum repens**, VI. 86b  
**Tritisporin**, V. 55a  
 " **Tritolo**," IV. 468d  
**Tritolylene**, I. 90a  
 " **Triton**," " **Triton B**," IV.  
467a; V. 101c  
 " **Trityl**" derivs. of glycerol,  
VI. 66a  
**Trogoderma kharpa**, V. 392d  
 " **Trolite**," IV. 466d  
 " **Tropacocaine**," I. 369a; III.  
224d  
**Tropaeolum majus**, IV. 335c;  
VI. 89a  
**Tropical bleach**, III. 02c  
**Tropilidene**, III. 635b  
**Tropine**, III. 225a  
**Tropopause**, I. 537c  
**Troposphere**, I. 537c  
**Trotyl** (see also T.N.T.), I. 406c  
**Truxillic acid**, III. 181b  
**Truxilline**,  $\alpha$ - and  $\beta$ -, III. 222d  
**Truxillines**, III. 224c  
**Truxinic acid**, III. 181b  
**Trypflavine** (see also Flavine),  
I. 134b, 125d  
**Trypanosoma**, effect of Mala-  
chite Green, IV. 30b  
 " **Trypsamide**," I. 487b  
 " **Trypsone**," I. 487b  
 " **Tryponarsyl**," I. 487b  
**Trypsin**, I. 600b; IV. 311d,  
319b  
**Tryptophan**, VI. 404b  
 -- in bran and cabbage, II. 59b,  
182d  
**Tsé-tiéou**, III. 33b  
**Tsuga canadensis**, II. 261b  
**Tsugaresinol**, VI. 202d  
**Tu**, III. 333b  
**Tubera jalapa**, III. 320c  
**Tubocurare**, III. 459c  
**Tubocurarine**, III. 459c  
**Tulipa gesneriana**, V. 330a  
**Tulipine**, V. 330a  
**Tung oil** (see also China wood  
oil; Oils, drying), I. 108b;  
II. 263a  
**Tungstates** in candle wicks, II.  
265b  
**Tungsten carbide**, II. 281a  
 -- carbonyl, II. 357a  
 --, detn., assay, I. 530c  
 --, --, gravimetric, II. 006a  
 --, -- in steel, I. 530c  
 --, --, volumetric, II. 068b  
 -- filaments, V. 171b, 178a  
 -- grain growth, V. 175b, 178b  
 -- hexachloride, action of Gri-  
nard reagent on, II. 357c  
 -- powder from WO<sub>3</sub>, V. 174b  
 --, --, pressing and sintering,  
V. 175a  
 --, qualitative reactions, II.  
554a, 556d, 575d  
 --, swaging and wire drawing,  
V. 176b  
 -- wire, drawn, V. 171d  
**Tungstic oxide**, prepn., V. 172d  
**Tunicin**, acetolysis, II. 442d  
**Turacin**, VI. 164c  
**Turanose**, II. 298b  
 " **Turkey-fat ore**," VI. 137a  
 -- Red oil, II. 52a, 420c; III.  
245d  
 --, --, in anti - dimming  
materials, III. 18d  
**Turneric**, III. 401c  
 -- paper, II. 52b  
**Turnerite**, II. 512b  
**Turpentine**, V. 415c; VI. 288c  
 -- oil, II. 249d  
 --, synthetic borneol from, II.  
316, 249c  
 --, --, camphor from, II. 249c  
**Turpethin**, III. 320d  
**Turquoise**, I. 264d  
 --, Alizarin, I. 232b  
**Tussah silk**, II. 18d; IV. 123d  
 " **Tutocaine**," I. 369a  
**Tvichosonic acid**, IV. 258a  
**Twice-coupling** components,  
VI. 195d  
**Twitcheil reagent**, ester prepn.  
with, II. 372b  
 -- reagents, reaction rates, VI.  
223a  
 " **Tyllithin**," I. 453b  
 " **Tylmarin**," antiseptic, IV. 29a  
**Tylose**, II. 480b  
**Typha-glucoside**, VI. 97b  
**Tyramine**, I. 147d; IV. 322b  
**Tyrosinase**, IV. 315b  
**Tyrosine**, I. 317b  
 --, 3:5-di-iodo-, I. 317b  
 -- in celery, II. 441b  
**L-Tyrosine**, N-methyl-, V. 517a  
**Tyrosine**, oxidation, II. 278b  
**Tysonite**, I. 655d

## U

- Ulex europaeus**, *U. spp.*, VI.  
125a  
**Ulexine** (see also Cytisine), VI.  
125b  
**Ulexite**, borax manufacture  
from, II. 46d, 49b  
 --, occurrence, II. 30c, 35b  
40a, d, 53b  
**Ullmannite**, I. 439d  
**Ulmus spp.**, oil from, IV. 278c  
**Ultrabasite**, V. 520a  
**Ultra-centrifuge**, III. 200a,  
604b  
**Ultra-filters**, II. 468d; III.  
282a  
**Ultramarine**, I. 201c, 583c  
 --, Cobalt, II. 25a; III. 218c  
 --, Gahn's, II. 25a  
**Ultra-microscope**, III. 280a  
**Ultraquinine**, III. 160d  
**Ultra-sonic waves**, effect on  
dispersions, III. 292b  
**Ultra-violet light**, disinfection,  
IV. 21d, foot-note  
**Umbelliferone**, V. 414c; VI.  
90a  
**Umbellulic acid**, III. 230c  
**Umbilicaria pustulata**, VI. 160c  
**Uncineol**, IV. 393a  
**Undecolic acids**, VI. 204a  
**Undecylenic acid** in cognac  
oil, II. 422a  
**n-Undecylenic acid**, VI. 204a  
**Universal buffer mixture**, II.  
123a  
 -- indicator, VI. 428d  
**Unkl**, V. 428c  
**Uracil**, IV. 332c  
 --, amino-, I. 020b  
 --, 5-hydroxy-, I. 030d  
 " **Uradal**," I. 141a  
**Uralorthite**, II. 512b  
**Uramil**, I. 628c  
**Uramino-acids**, I. 320b  
**Uranine**, V. 272d  
**Uranin**, phosphor, II. 224b  
**Uraninite**, II. 106a; VI. 154d  
**Uranium**, detn., assay, I. 530c  
 --, --, electrodeposition, II.  
702c  
 --, --, gravimetric, II. 006d  
 --, --, potentiometric, II. 708c  
 --, --, volumetric, II. 068b  
 " **Uranium micas**," I. 558a  
**Uranium**, qualitative re-  
actions, II. 555d, 556d, 575d  
 -- vanadate in carnottite, II.  
392d  
**Uranous salts**, qualitative re-  
actions, II. 575d  
**Uranyl salts**, qualitative re-  
actions, II. 670a  
**Urari**, III. 459b  
**Urbain charcoal**, II. 317a  
**Urea fertiliser**, V. 66a  
 --, reaction with bromal, II.  
106b  
**Urease**, IV. 311d, 315a  
 --, antidote to phosgene, II.  
322a  
**Urethidin**, II. 387d; VI. 97b  
**Urethoxin**, II. 387d; VI. 97b

- Urethane**, *p*-acetoxyphenyl-, I. 73b  
 —, double salt, with calcium bromide, II. 235a  
**PseudoUric acid**, I. 629b  
**Uric acid**, qualitative reactions, II. 570d  
**Uricase**, IV. 315b  
**Uridine**, VI. 97b  
**"Uritone,"** I. 326a  
**Urobilin**, I. 200c, 691c  
**Urobilinogen**, I. 691a, d  
**Uronic acid**, II. 207b  
**Uroporphyrin**, VI. 162a  
**Urorescin**, VI. 464a  
**"Urotropin,"** "urotropine," I. 326a; IV. 27d; V. 320b  
**"Urotropine quinade,"** III. 33d  
**Ursocolic acid**, I. 600a  
**Urson**, ursone, I. 600c; III. 435c  
**Urtite**, I. 450b  
**Uteroverdin**, I. 602a  
**Uvarovite**, V. 429b  
**Uzaren**, II. 380d  
**Uzargenin**, II. 382a  
**Uzarin**, II. 386d; VI. 97c
- V**
- Vacciniin**, vaccinin, III. 414d; V. 328b; VI. 97c  
**Vaccinium myrtillus**, VI. 92b  
 — *spp.*, I. 688c; III. 414b  
 — *vitis-idea*, V. 328a; VI. 97c  
**Vacuum pans**, IV. 400a  
**Valenta** test of butter, II. 166c  
**Valentinite**, I. 439d, 440a  
**Valeric acid**, antiseptic, IV. 28b  
 —,  $\alpha$ -amino- $\delta$ -guanidino-*n*-, I. 459d  
 —,  $\alpha$ - $\delta$ -diamino-, I. 459d  
 — in caffeeol, II. 198b  
**•Valeronitrile**, II. 172d  
**isoValerylurea**,  $\alpha$ -bromo-, II. 118d  
**Valonia**, IV. 270d  
**Vanadates**, qualitative reactions, II. 555b, 556d, 573d  
**Vanadium** as trace element, I. 510d  
 — carbide, II. 281a  
 —, detn., colorimetric, II. 673b  
 —, —, gravimetric, II. 601c  
 —, in steel, I. 530d  
 —, —, potentiometric, II. 708c  
 —, —, volumetric, II. 668c  
 —, —, in steels, II. 668d  
 — in canarin production, II. 261c  
 — carnotide, II. 392d  
 — porphyrins, VI. 165b  
 — pentoxide catalyst in SO<sub>3</sub> production, II. 423c  
 —, oxidising catalyst, II. 427d  
 — sols, III. 289c  
**Vanaashpati**, V. 531d  
**"Vandura"** or "*Vandura*" rayon, V. 115b  
**Vanilla** essence, detn. of coumarin in, III. 412d  
**Vanillin** from isoeugenol, IV. 399a  
**Vanillylamine**, formation from capsacine, II. 272c  
**Van't Hoff** equation of change of equilibrium with temperature, II. 588a
- Vapour** condensation on nuclei, IV. 97c  
 — pressures of immiscible liquids, IV. 35a  
 — — miscible liquids, IV. 30d  
 — — partly miscible liquids, IV. 35d  
**Vapours**, organic, gasometric detn., II. 684d  
**Varentrapp's** reaction, VI. 177b  
**Variamine Blue Salt**, III. 581c  
**Varianose**, V. 58a  
**Variegated** copper-ore, II. 32d  
**Vat** and vatting dyes, IV. 129b  
 — colours, anthraquinone, intermediates, I. 408a  
 — dye derivs., IV. 129c  
 — dyes, I. 205c; IV. 129a  
 —, solubilised, I. 428d  
**Vautin** electrolytic cell, III. 57a  
**Vein-tin**, II. 119c  
**"Velan P.F."**, V. 197c  
**Vello** glass - tube drawing machine, V. 591a  
**Vellosine**, V. 504a  
**Velvet** ore, VI. 101a  
**Veratric acid**, IV. 397a  
 — from capsacine, II. 272c  
**Veratrole**, II. 431b  
**Veratrum album**, V. viride, II. 1d; VI. 200c  
**Verbenalin**, VI. 97c  
**Verbenaldehyde**, VI. 97c  
**Verbena off.**, VI. 97c  
**Verdian**, III. 107b  
**Verdigris**, I. 54b  
**Verdizers**, III. 354d, 356a  
**Veridian**, IV. 279c  
**Vermillion**, American, I. 304c; III. 113b  
 — in prepn. of Brunner's salt, II. 119b  
**Vernine**, VI. 89b  
**"Veronal,"** I. 623a  
**Vert Arnaudon**, III. 100a  
**Verticilline**, V. 330b  
**Verticine**, V. 330b  
**Vert Plessy**, III. 100a  
**"Vesalvine,"** I. 326a  
**Vesicants** in warfare, III. 7d  
**Vestrylamine**, formation, II. 393c  
**Vesuviarite**, II. 234b; VI. 414a  
**Vetch** seeds, glycoside, III. 326c  
**Viburnin**, II. 1c  
**Vicat** plunger, II. 144a  
**Vicianase**, IV. 314b  
**Vicianin**, VI. 97c  
 —, sugar in, II. 300b  
**Vicianose**, II. 298b; VI. 46a  
**Vicia spp.**, I. 248b, 511c, 658d; III. 554c; VI. 97c  
**Vicin**, III. 554c  
**Vicine**, VI. 97d  
**Vieille** test, IV. 534b  
**Vietinghoffite**, II. 512c  
**Vining**, III. 414a  
**Vining** powder, IV. 554c  
**Villalstonine**, I. 263d  
**Vinasses**, VI. 41b  
**Vinegar**, I. 44b  
 —, analysis, I. 47a, 53b; V. 297a  
 —, artificial, and vinegar essence, I. 46c
- Vinegar**, preservative, IV. 28a; V. 297a  
 —, cider, date, distilled, grain, glucose, I. 44a, 46a  
 —, spirit, sugar, white wine, wine, and wood, I. 44c, 46c  
**"Vinethene,"** I. 388a; IV. 53a  
**Vinyl acetate**, I. 37d, 91d  
 — resins, I. 90c, 92a, 93c  
**Vinylacetonitrile**, I. 258b  
**Vinylacetylene**, I. 87c  
 —, halogen derivs., I. 89a  
 — resins, I. 88b  
**Vinyl allyl ketone**, I. 90b  
 — chloride, I. 87d, 90d; IV. 374c  
 — esters, I. 92b  
 — ether rosins, I. 93c  
 — ethers, I. 35a, 92d  
 — ethinyl-dimethyl-carbinol, I. 88d  
**Vinylformic acid**, I. 137a  
**Vinyl halide** resins, I. 90c  
**Vinylite**, I. 90c  
**Vinyl phenols**, I. 91c  
**Vinylquinoludoneoxime**, III. 159b  
**"Vinyon,"** V. 120b  
**Violanin**, III. 554c; VI. 98a  
**Violanthrene**, BS, CD, R extra, I. 424a  
**Violanthrone**, I. 205c, 413d  
**Violaquercitrin**, VI. 95a, 98a  
**Violaxanthin**, II. 398d; III. 181d  
**Violerythrin**, 401a  
**Violet**, Alkol B, I. 232d  
 —, Alizarin Cyanol, R, I. 231b  
 —, — Direct, I. 232b  
 —, — R, I. 406c  
 —, Amethyist, I. 576c  
 —, Aniline, I. 577c  
 —, Anthraquinone, I. 232a, 405c  
 —, Caledon, BN, XBN, I. 417b, c  
 —, Brilliant, R, I. 410b  
 —, Cibacnone, BW, I. 424d  
 —, Indanthrene, B extra, RN and RR, I. 424a, 396b  
 —, — Brilliant, 3B, I. 424b  
 —, Iris, I. 576c  
 —, Methylene, BN, I. 576c, 577a  
 —, Neutral, I. 569b  
 —, Perkin's, I. 376d, 504c, 577b  
**Violets**, Acid, I. 120a  
**Violet**, Williamson's, III. 473b  
**Violuric acid**, I. 246a, 626c  
**isoVioluric acid**, I. 246a  
**Violutin**, VI. 98a  
 —, sugar in, II. 300b  
**Violutoside**, VI. 98a  
**Viper venom**, II. 24c  
**Viridanthrene B**, I. 424a  
**Viridobufagin**, II. 388c  
**Viridobufotoxin**, II. 388c  
**"Viscin,"** I. 692d  
**"Viscoloid,"** II. 443b  
**Viscose** (dextran), III. 567c  
 —, cellophane from, II. 422d, 452b, c  
 —, dispersion, II. 459c  
 —, manufacture, II. 342c, 465b; V. 117c  
 —, ripening, V. 118c, 120d  
 —, silk, see Rayon, viscose  
 —, spinning, V. 119a, 127b  
 —, coagulating baths, V. 120a  
**Viscosity**, detn. and specification, II. 470b  
 — of starch, II. 302c

- Vitamin A** in bran, cacao butter and maize, II. 62*b*, 186*a*, 482*b*  
 — of cod-liver oil, III. 248*b*  
 — relation to carotenoids, II. 402*b*  
 —, replacement by carotene, II. 394*d*  
 —  $B_1$ ,  $B_2$ , in yeast, II. 98*c*, 103*d*  
 —  $B$  in *hman*, chocolate and rice, II. 62*b*; III. 88*a*; II. 498*b*  
 —  $B_1$ , I. 371*c*, 583*b*; VI. 138*d*  
 —  $B_2$ , II. 287*b*; VI. 91*a*  
 — in bran and maize, II. 62*b*, 482*b*  
 —, ribose in, II. 287*b*  
 —  $B_3$ , VI. 139*a*  
 —  $C$ , I. 501*c*  
 — in cabbage and paprika, II. 183*b*, 274*d*  
 —  $D$  in cacao shell fat, II. 186*d*  
 — of cod-liver oil, III. 249*b*  
 —  $D_1$ , II. 202*c*  
 —  $D_2$ , II. 201*c*, 202*c*; III. 249*b*  
 —  $D_3$ , II. 203*a*; III. 249*c*  
 —  $E$  activity of cod-liver oil, alleged, III. 250*a*  
 — in maize and wheat germ, II. 428*b*, 505*c*  
**Vitamins  $B_1$ - $B_6$** , I. 583*b*  
 — in butter, carrots and cereals, II. 161*b*, 168*a*, 404*a*, 486*d*  
 — hydrogenated fats, VI. 185*d*  
 — wheat and yeast, II. 505*c*, 103*d*  
**Vitellin**, v. membrane, IV. 255*d*, *b*  
 — in maize, II. 481*d*  
**Vitexin**, VI. 95*c*  
**Vitis spp.**, VI. 92*c*, 127*d*, 130*c*  
**Vitrain**, V. 350*d*  
**Vitritite**, V. 351*b*  
**Vitriol**, blue, II. 25*b*; III. 357*b*  
 —, brown oil of, II. 119*a*  
 —, Cyprian, *see* Vitriol, blue.  
 —, white, VI. 125*b*  
 —, zinc, *see* Vitriol, white.  
**Vitrum antimonii**, I. 447*b*  
**Vivianite**, II. 25*b*; IV. 335*c*  
**Voelckerite**, I. 449*d*  
**"Vol."** I. 586*d*  
**Volatility**, relative, IV. 34*c*  
**Volemitol**, II. 290*d*  
**Volgerite**, I. 439*d*  
**Vonges dynamite**, IV. 240*d*  
**Vorobyevite**, I. 684*c*  
**"Voxsan"** disinfectant, IV. 20*d*  
**Vulcanisation accelerators**, I. 12*b*, 20*c*; II. 157*a*  
 —, cold, carbon disulphide in, II. 343*b*  
 —, —, tetrachloride in, II. 350*b*  
 —, xanthates in, II. 343*d*  
**Vulgarobutotoxin**, II. 388*b*  
**"Vulpinite,"** I. 372*c*  
**Vuzin**, III. 166*b*, 168*b*  
**W**  
**Wad**, II. 26*b*, 314*b*; III. 214*b*  
**Wagner-Meerwein rearrangement**, II. 238*d*  
**Wagner's reagent**, I. 235*c*  
**Walnut oil**, IV. 86*b*  
**Walsrode powder**, IV. 530*a*  
**Warp dyeing**, IV. 130*c*  
**Washers**, *see* Absorption.  
**Waste**, II. 512*b*  
**Waste-heat boilers**, V. 441*b*, 471*a*, 494*d*  
**Water**, *detn.* in grain, dielectric method, II. 710*a*  
 —, with calcium carbide (*see also* Water vapour, *detn.*), II. 82*c*  
 —, "free," VI. 206*a*  
 — gas (*see* Carburetted water gas; Coke manufacture; Fuel; Gas, coal; Gas, water).  
 — reaction, catalysed, VI. 379*d*  
 — hemlock, cicutoxin in, III. 120*b*  
 — in butter, II. 159*c*  
 — molecule, catalysis by, VI. 253*c*  
**Waterproof fabrics**, heavy, V. 195*d*  
**Waterproofing**, *casem* in, II. 414*d*  
 — with cellulose nitrate, drying oils, rubber and r. latex, V. 194*a*  
 — synthetic resins and waxes, V. 105*a*, 100*a*  
**Water purification** (*see also* Disinfectants), I. 201*b*; II. 320*a*  
 — repellent fabrics, V. 196*d*  
 — with soft handle, V. 197*c*  
**Waters**, chalybeate, bacterial oxidation, II. 26*a*  
**Water sterilisation**, chlorine treatment, III. 30*c*  
 — vapour, *detn.* (*see also* Water *detn.*), II. 685*c*  
**Wattle bark**, I. 11*c*  
**Wavellite**, I. 264*d*  
**"Wax, China,"** VI. 496*c*  
**Wax**, Chinese, VI. 496*b*  
 —, insect, VI. 496*b*  
 —, cotton, V. 141*d*  
 —, East Indian (Bees), V. 530*b*  
 —, fig, V. 171*a*; VI. 123*b*  
 —, flax, V. 202*c*  
 —, Getah, or Gondang or Java, V. 171*a*; VI. 123*b*  
 —, insect, VI. 496*b*  
 —, Kondang, or Sumatra, V. 171*a*; VI. 123*b*  
 —, vegetable, analysis, II. 202*b*  
**Weather-Omster**, I. 167*d*  
**Webnerite**, I. 370*d*  
**Websterite**, I. 280*a*  
**Wedekind's reaction**, III. 23*c*  
**Weighing** in analysis, II. 542*c*  
**Weighting fabrics**, IV. 144*a*; V. 187*a*  
**Weissensteiner persulphate cell**, VI. 312*b*  
**Weissglitzgerz**, IV. 590*d*  
**Welding**, atomic hydrogen, VI. 334*b*  
**Weldon mud**, III. 41*a*  
 — process, III. 41*a*  
**Welsbach mixture**, V. 482*d*  
**Wenk den**, V. 72*c*  
**Werner co-ordination compounds**, III. 327*c*  
**Weston cell**, II. 194*c*  
**"Westron,"** *see* Ethane, tetra-chloro-  
**"Westrosol,"** I. 90*c*; II. 428*d*  
**Wet-on-wet painting**, IV. 86*b*, 90*c*  
**Wetter astralit**, IV. 554*b*  
**Wetting agents**, II. 179*b*, 391*a*; IV. 280*a*  
 —, sulphonated fatty alcohols, VI. 183*c*  
 —, theory, VI. 508*c*, 509*a*  
 —, triethanolamine, I. 307*a*; IV. 350*b*  
 —, Turkey Red oil, II. 421*d*  
 — out agents, *see* Wetting agents.  
**Weyl's extractor**, IV. 577*c*  
 — test for creatinine, III. 417*d*  
**Whale oil**, V. 229*b*  
 — for paints, IV. 85*b*  
 —, hardened, II. 420*d*  
**Wheat**, II. 504*a*  
 —, Durum, II. 70*c*  
 — flour, baking value, II. 504*c*, 505*d*  
 — germ, effect on flour, II. 505*c*  
 — oil, II. 505*d*  
 —, vitamins in, II. 505*c*  
 — straw, II. 500*b*; IV. 595*a*  
**Wheel-ore**, II. 53*d*  
**Whetstones**, I. 4*c*; VI. 279*b*  
**Whin**, VI. 125*a*  
**Whinstone**, III. 571*b*  
**White**, alumina, I. 290*d*  
 —, American Paris, I. 304*c*  
 —, Antimony, I. 439*d*, 440*c*  
 — argol, I. 401*d*  
 — arsenic, I. 168*c*, 473*a*  
 — baryte (*see also* Baryte; Blanc fixe; White, Permanent), I. 851*d*  
 — boil in degumming silk, II. 18*b*  
 — ditauy, III. 602*b*  
 — flake, I. 609*d*  
 — mundic, I. 400*a*  
 — ore, II. 519*d*  
 — Paris, II. 518*c*  
 — Pearl, I. 699*d*; II. 3*a*  
 — Permanent, I. 642*a*, 651*c*, 651*d*  
**Whiting electrolytic cell**, III. 50*a*  
**Whitneyite**, IV. 55*b*  
**Whortleberry**, I. 688*c*; III. 414*b*  
**Widia**, III. 217*b*, *c*  
**Wiesenerz**, II. 20*a*  
**Wildermann electrolytic cell**, III. 50*c*  
**"Wild ginger,"** I. 498*d*  
**Wiley's extractor**, IV. 577*b*  
**Willemite**, V. 413*a*  
**Willessen fabrics**, W. papers, V. 191*c*; III. 355*a*  
**"Wilmit,"** I. 251*b*, 253*b*, 277*c*  
**Winch machines in dyeing**, IV. 130*b*  
**Wine**, III. 558*d*  
 —, citric acid in, III. 190*b*  
**Wines in brandy production**, II. 04*a*  
 —, purification with ivory black, II. 311*d*  
**Wintergreen oil**, I. 692*b*  
**Wintering oils**, V. 232*d*  
**Winter oils**, IV. 253*a*  
**Winter's grass**, citronella oil from, III. 191*a*  
**Wisnut**, I. 694*b*

**Witch-hazel**, VI. 177a  
**Withamite**, IV. 320d  
**Witherite**, I. 631b, 638a  
**"Witherite, low-grade,"** I. 651d  
**"Witt's rule"** of colour origin, III. 808b  
**Wobbe index**, V. 246c  
**Wöhlerite**, III. 310a  
**Wohlwill process**, VI. 108b  
**Wolfram**, II. 198d  
**Wolframite**, V. 173a  
**Wolfsbergite**, I. 439d; II. 518a; V. 520c  
**Wollastonite**, II. 227c  
**Wollney's extractor**, IV. 579a, 580b  
**Wood**, coal formation from, V. 330a  
 — fuel, V. 336d  
**Wood-naphtha**, I. 183a; III. 558a  
 — pulp for viscose, II. 405b; V. 117c  
**Wood's glass** - tube drawing machine, V. 589d, 590b  
 — metal, I. 698d  
**Wood smoke preservative**, V. 200d  
 — spirit disinfectant, IV. 26b  
**Wood-tin**, II. 419c  
**Wool**, action of acids and alkalis, V. 108b  
 —, — halogens, V. 111b  
 —, — inorganic salts, V. 111c  
 —, — organic compounds, V. 111d  
 —, — oxidising agents, V. 111a  
 —, — reducing agents, V. 110c  
 —, — water and steam, V. 106a, 107c  
 — amino-acid analysis, V. 100b  
 — bleaching, II. 12b; V. 110d  
 —, casein, artificial, II. 416a  
 —, chlorinated, IV. 123c; V. 111b  
 —, conductivity, electrical and thermal, V. 107b  
 —, crimpiness in, V. 96d  
 —, degreasing, trichloroethylene, I. 102d  
 —, dyeing, IV. 122d, 130b  
 —, elastic properties, V. 104c  
 — fat (see also Cholesterol), VI. 135c  
 — fibres, dimensions, properties and composition, V. 90a  
 —, medullated, V. 97c  
**Woolf's electro-zone**, IV. 21b  
**Wool, greasy**, analysis, V. 90c  
 —, isoelectric point, V. 108a  
 —,  $\alpha$ - and  $\beta$ -keratin, X-ray analysis, V. 102b  
 —, "mercerising," V. 110b  
 —, "pink rotted," V. 98b  
 —, polypeptide chains in, V. 101d  
 —, printing, IV. 186a  
 —, slipe, II. 13d  
 —, stoving, II. 10c  
 —, sulphur content, V. 98d  
 —, "unshrinking," IV. 123c  
 —, waste fertiliser, V. 66c  
 —, water adsorption, V. 103a  
**Woorali**, Woorara, Woorari, III. 459b  
**Worm**, pink boll, V. 139f

**Wormseed**, V. 263c  
 — oil, American, I. 501a; III. 24d  
 —, cineole in, III. 179b  
**Wormwood**, oil, I. 5a  
**Wort**, II. 86d, 95c  
**Wound** "hormone" of plants, VI. 138d  
**Wrightine**, III. 321d  
**Wuchuyine**, IV. 415d  
**Wüstite**, II. 229c  
**Wurtzite**, IV. 307d; VI. 136d  
**Wurtz reaction**, II. 363d

## X

**Xanthates** as fungicides, II. 343d  
 — in vulcanisation, I. 12c; II. 343d  
 —, manufacture, II. 342a, 343d  
**Xanthation**, viscose process, II. 405b; V. 118a  
**Xanthene** in tea, II. 197a  
**Xanthin**, dye, I. 133b  
**Xanthine**, II. 108a; VI. 98b, 151d  
**Xanthochroite**, VI. 137a  
**Xanthocridol**, IV. 333d, 334a  
**Xanthogenates**, see Xanthates  
**Xanthone**, V. 55d  
 —, 1:7-dihydroxy-3-methoxy-, V. 516d  
 —, 1:3:7-trihydroxy-, V. 516c  
**Xanthophyll**, II. 17b, 308a  
**Xanthopurpurin**, I. 212d, 220c  
**Xanthoquinic acid**, III. 178c  
**Xanthoresinotannol**, I. 618b  
**Xanthorhamnin**, II. 120c; VI. 98a  
**Xanthorrhæa spp.**, varnish gums, I. 12b, 618a  
**Xanthosinase**, IV. 315a  
**Xanthosine**, VI. 98b  
**"Xara,"** I. 517d  
**Xenene**, IV. 10a  
**Xenotime**, II. 512c; IV. 245c, 321c  
**"Xeroform,"** I. 701a  
**X-ray**, see X-Ray  
**Xylan**, II. 287a, 303c; VI. 201a  
**Xylanase**, III. 542c  
**Xylan** in cellulose detn., II. 402c  
**Xylene**, I. 671b  
**o-Xylene**, I. 466d, 671d  
**m-Xylene**, I. 466d, 671d  
**p-Xylene**, I. 466d, 671d  
**Xylene**, carcinogenic compounds from, II. 378c  
**m-Xylene**, from azafurin, II. 307a  
**Xylene**, nitro-, I. 677a  
 —, trinitro-, IV. 474b  
**Xylenols** from crude phenol, II. 304b  
**m - Xylidene**, dehydrothio-, II. 553c  
 —, isodehydrothio-, III. 553c  
**Xylidine**, I. 573b  
**d-Xyloose**, II. 288c  
**"Xylonite,"** II. 443b, 480b  
**Xylose**, II. 282b, 287a  
 —, dibenzoylgluco-, VI. 87c  
 — from bran, II. 62d  
**Xylyl bromide**, prepn., III. 17b

## Y

**"Y" alloy**, I. 252b, 277a  
**Yams**, IV. 10a  
**Yarrow**, I. 119d  
**Yeast**, see also Fermentation, alcoholic  
 —, brewer's, II. 98b; VI. 511a  
 —, cider, III. 125d  
 —, dried, IV. 597a; V. 15a, 18d  
 — enzymes, II. 99d, 103c; V. 13b  
 — extract, alcohol formation in, V. 28a  
 —, co-zymase from, V. 16a  
 — in bread, II. 75a  
 — juice, V. 13c  
**Yeasts**, wild, II. 91a  
**"Yel butter,"** I. 654a  
**Yellow**, Acridine, I. 131c, 134a  
 —, Alcol, 3G, GC, R, WG, I. 416c, 418d, 232a  
 —, Alizaranthrene, I. 419d  
 —, Alizarin, and I. 206d, 233b, 207a  
 —, C, V. 417a  
 —, Antimony, I. 447c  
 —, Bark, II. 234b  
 —, Benzo Eust, (GL), IV. 222a  
 —, Benzoin, I. 229b  
**"Yellow berries,"** VI. 98a  
**Yellow**, Brilliant, IV. 221b  
 —, Buttercup, III. 113c  
 —, Cadmium, II. 194a, d  
 —, Caledon, 3 G, I. 396d, 416b  
 —, G, I. 419d  
 —, Cassel, II. 418b  
 —, Chinese, III. 33d  
 —, Chrome, III. 96d, 112a  
 —, American, III. 112b  
 —, Cibonone R, I. 423c; II. 25b, 119b  
 —, Cobalt, III. 210b  
 —, Cologne, III. 112a  
 —, Cutch, II. 433b  
 —, Dispersol, 3 GS, I. 41a  
 —, Erweco Fast, G, I. 419b  
 —, Helio Past, I. 233a  
 —, Höchst, VI. 450d  
 —, Hydron, G, I. 423b  
 —, Indanthrene, G, GF and 3GK, I. 394d, 419c, 420c  
 —, GN, 3R and 3RT, I. 390c, 418d, 421d  
 —, Golden, GK, I. 426b  
 —, Indian, III. 219b; IV. 405a  
 —, VI. 424b  
 —, Indigo, VI. 439a  
 —, 3G Ciba, VI. 450b  
 —, Indolenine, III. 519d  
 —, Ionamine, MA, I. 40c  
 —, Isatin, VI. 304b  
 —, King's, I. 479b; III. 33d  
 —, Leather, I. 133b  
 —, Leipsic, III. 112a  
**"Yellow, Lemon,"** I. 642c; III. 111a  
**Yellow**, Mémimée's, I. 447c  
 —, Mikado, IV. 221c  
 —, Mineral, II. 418b  
 —, Montpellier, II. 418b  
 —, Naphthamine, G, IV. 221c  
 —, Naphthol, S, III. 417d, f-n.  
 —, Naples, I. 447d; V. 531d  
 —, Nitrazine, II. 639c  
 —, indicator, VI. 428d  
 —, Ochre, II. 473b  
 —, Paradone, GC, 5GK, I. 419c, 410c  
 —, Paris, III. 112a

**Yellow**, Patent, II. 418b  
 —, Philadelphia, I. 133b  
 "Yellow prussiate of potash,"  
 III. 465*c*, 474*d*  
**Yellow**, Pyrazolanthrone, I.  
 415*c*  
**Yellows**, Acid, I. 120*a*  
 —, Hansa, IV. 235*a*  
**Yellow**, Soledon, G, I. 429*b*  
 — sulphide of arsenic, I. 479*b*  
 —, Turmeric, III. 461*c*  
 —, Turner's, II. 418*b*  
 "Yellow, Ultramarine," I.  
 642*c*; III. 111*d*  
**Yellow**, Vitolin, I. 133*b*  
 —, Zinc, III. 96*d*, 113*c*  
**Yenite**, VI. 415*b*  
**Ylang-ylang** oil, II. 261*b*  
**Yoder's** extractor, IV. 585*d*  
**Yolk** in raw wool, II. 12*b*  
**Yonckite** anti-grison, IV. 556*a*  
 "Yonckite 10 bis" and "13,"  
 IV. 464*d*  
**Ytterbite**, II. 511*b*; IV. 321*c*  
**Ytterolimenite**, II. 512*c*  
**Yttrialite**, II. 512*b*  
**Yttrotalite**, II. 512*c*; IV.  
 321*c*

**Z**

**Zaffler** (Zaffre), III. 219*c*  
**Zapote** blanco, II. 418*a*  
**Zeaxanthin**, II. 398*d*; III.  
 181*d*  
 — in red pepper, II. 272*b*  
**Zein**, II. 481*d*  
**Zeisel** methoxyl group detn.,  
 II. 621*d*  
 —, —, micro-, II. 633*d*  
 "Zelan A," V. 197*c*  
**Zenker** formal solution, IV.  
 255*c*  
**Zeolites**, I. 261*d*, 291*c*; II.  
 229*b*  
 — in base-exchange reactions,  
 VI. 218*b*, 219*a*  
**Zeotropic** mixtures, IV. 51*b*

**Zerewitinoff's** detn. of active  
 hydrogen, II. 624*c*  
 — hydroxyl detn., II. 624*c*  
**Zibda**, II. 108*c*  
**Zibetone**, III. 194*b*  
**Ziegelerz**, III. 459*a*  
**Zierin**, VI. 98*b*  
**Zinc** acetate in respirators,  
 III. 20*c*  
 —, reaction with bornyl  
 chloride, II. 254*b*  
 — alkyls, reaction with carbon  
 dioxide, II. 363*c*  
**Zincamines** in respirators,  
 III. 20*c*  
**Zinc** as trace element, I. 510*d*  
**Zincates** in respirators, III.  
 20*c*  
**Zinc** blende, II. 19*a*  
**Zinc-cadmium** alloys, electro-  
 deposition of, IV. 270*c*  
 — carbide, II. 281*c*  
 — carbonate, catalyst for  
 methanol prepn., II. 350*b*  
 — for glassmaking, V. 558*c*,  
 561*b*  
 — cerium alloy, II. 507*d*  
 — chloride disinfectant, IV. 24*a*  
 —, —, electrolysis, III. 57*d*  
 — chromate, III. 96*d*  
 — chromite, catalyst for  
 methanol prepn., II. 350*b*,  
 425*c*  
 — chromium alloy, III. 103*d*  
 — cyanide, III. 487*c*  
 —, detn., assay, I. 531*a*  
 —, —, electrodeposition, II.  
 702*d*  
 —, —, gravimetric, II. 580*c*  
 —, —, hydrogenation method,  
 VI. 361*d*  
 —, — in food, II. 292*d*; V. 292*d*  
 —, —, micro-method, II. 633*c*  
 —, —, potentiometric method,  
 II. 708*d*  
 —, —, spectroscopic, II. 692*a*  
 —, —, volumetric, II. 698*d*  
 —, drop reaction, II. 581*c*  
 —, electrodeposition, IV. 267*d*

**Zinc** ethyl, reaction with acety-  
 lene, II. 281*c*  
 — ferrocyanide, III. 475*b*  
 — in rice, II. 496*c*  
**Zincite**, relation to bromellite,  
 II. 106*c*  
**Zinc** methoxide, catalyst in  
 acetic acid prepn., II. 350*d*  
 — oxide pigment, II. 444*b*, 473*a*  
 — phosphate, hydrated, VI.  
 265*d*  
 —, qualitative reactions, II.  
 553*c*, 567*c*; VI. 209*b*  
 —, —, rare metals present,  
 II. 555*d*, 556*d*  
 — spar, II. 201*b*  
 — spinel, I. 264*c*; V. 413*a*  
 — uranyl acetate, reagent, II.  
 584*a*  
**Zingerone**, V. 534*c*  
**Zingiberene**, V. 535*d*  
**Zingiber officinale**, Z. spp., V.  
 533*b*, 535*d*  
**Zircon**, VI. 288*d*  
**Zirconium**, II. 511*c*  
 — carbide, II. 281*a*  
 —, detn., gravimetric, II. 597*c*  
 —, —, volumetric, II. 600*b*  
 —, drop reaction, II. 581*c*  
 — oxide, II. 67*c*  
 —, qualitative reactions, II.  
 554*a*, 556*b*, *d*, 571*d*  
**Zirkite**, I. 585*c*  
**Zonalite**, II. 227*c*  
**Zoomaric** acid, III. 247*b*  
 "Zotos," I. 70*d*  
**Zulkowski's** extractor, IV.  
 577*b*  
**Zwitterion**, constitution, I,  
 323*b*  
**Zwitterions**, III. 287*a*  
 "Zyklon B," V. 304*c*  
**Zymase** in dough, II. 70*b*  
 — yeast juice, V. 13*c*  
**Zymin**, V. 15*a*, 20*b*  
 —, inactivation by washing, V.  
 18*d*  
**Zymohexase**, V. 25*d*; VI. 76*d*  
**Zymosterol**, IV. 325*c*